UNITED STATES DEPARTMENT OF COMMERCE
JESSE H. JONES, Secretary
NATIONAL BUREAU OF STANDARDS
Lyman J. Briggs, Director

✦

Journal of Research

of the

National Bureau of Standards

✦

Volume 32, Number 4

April 1944

[Published with approval of the Director of the Budget]

UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON : 1944

For sale by the Superintendent of Documents, U. S. Government Printing Office
Washington 25, D. C. - Price 30 cents, $3.50 per year on subscription

The prices of the separate Research Papers appearing in this JOURNAL are given on the front cover page. If 100 or more copies of any separate are ordered, a discount of 25 percent is allowed. Those who desire copies of separate Research Papers should send their orders and remittances without delay to the Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C. This will aid him to determine the number of copies to be printed for sale. Research Papers are not printed from electrotypes, and usually no more reprints can be had when the first and only printing is exhausted.

MATHEMATICAL TABLES

A list of the mathematical tables now obtainable from the National Bureau of Standards is printed on pages 3 and 4 of the JOURNAL cover. New tables will be announced from time to time as they become available.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1580

Part of Journal of Research of the National Bureau of Standards, Volume 32, April 1944

EFFECT OF SODIUM CHLORIDE ON THE pH OF *p*-PHENOLSULFONATE BUFFERS FROM 0° TO 60° C

By Roger G. Bates and S. F. Acree

ABSTRACT

The electromotive forces developed between the hydrogen and silver chloride electrodes of galvanic cells which contained 12 mixtures of potassium *p*-phenolsulfonate, sodium hydroxide, and sodium chloride were measured from 0° to 60° C at intervals of 5 degrees. Sufficient alkali was used to neutralize half of the phenolsulfonate in each solution. The molal ratios of sodium hydroxide to sodium chloride were 10, 4, 2, and 1. The pH of each solution, and of six phenolsulfonate buffers without sodium chloride, was determined. Equations are given to represent the change of pH at each of th 13 temperatures with molality of sodium chloride. It is shown that the ionic strength and pH of unknowns may be obtained approximately, and the usual salt errors largely eliminated, from emf measurements on two portions of the unknown solution to which different amounts of sodium chloride have been added.

CONTENTS

	Page
I. Introduction	131
II. Experimental procedure and the calculation of pH	132
III. Equations for the salt effect	136
IV. Standard buffer solutions	138
V. Estimation of the ionic strength and pH of unknown mixtures of potassium *p*-phenolsulfonate and sodium hydroxide	140
VI. References	143

I. INTRODUCTION

Buffers composed of potassium *p*-phenolsulfonate and sodium hydroxide are satisfactory for the control of alkalinity and for the calibration of pH equipment in the slightly alkaline region between pH 8.5 and pH 9.0 [1].[1] Potassium phenolsulfonate is easily purified, is anhydrous and nonhygroscopic [2], and its aqueous solutions are stable from 0° to 60° C when reasonable protection from strong light is provided.

Cells with hydrogen and silver chloride electrodes were used in the determination of the second dissociation constant of *p*-phenolsulfonic acid and the pH values of phenolsulfonate-chloride mixtures [1]. The cells contained known concentrations both of the buffer salts and of sodium chloride.

[1] Figures in brackets indicate the literature references at the end of this paper.

In the list of provisional pH standards given in an earlier publication [3], the pH values of buffers containing chloride were reported. These buffer solutions can therefore be used in hydrogen–silver-chloride cells without liquid junction, as well as in cells which involve a liquid junction and calomel electrode. In most practical work, however, sodium chloride serves no useful purpose in a standard buffer solution apart from its small influence on the pH value and from the usually negligible increase in precision of the emf measurement which results from the increased conductance of the mixture. The effect of the salt upon the buffer capacity, stability, and other desirable properties of the solution is so small as to be without significance. If the influence of the sodium chloride upon the activity coefficients and pH values of the buffers were known, the inconvenience of adding chloride to buffers prepared as calibration standards could be avoided.

The effect of neutral salts upon the behavior of buffer solutions is of further interest in its bearing on the spectral properties of mixtures which contain tautomeric ions in homogeneous equilibrium. It has been shown [2] that phenolsulfonate buffers have characteristic absorption bands in the ultraviolet region of the spectrum similar to those of indicator ions and molecules in the visible region. Furthermore, studies of the effect of salts on the absorptive properties of indicator ions and molecules suggest that the activity coefficients of these tautomeric ions change normally with increase of ionic strength up to about 0.5, but specific salt effects larger than the experimental errors are observed if the indicator is dissolved in solutions which are 0.5 to 2 *M* with respect to various salts [4, 5].

This paper reports a study of 12 equimolal mixtures of potassium *p*-phenolsulfonate and potassium sodium *p*-phenolate sulfonate with 4 different molal ratios of sodium chloride to buffer salt at 5-degree intervals from 0° to 60° C. Electromotive-force measurements were made at the 13 temperatures, and the pH values were calculated. The influence of sodium chloride on the pH was shown to be a "normal salt effect." Equations were formulated to express the observed change of pH with molality of sodium chloride, and the calculated pH values of *p*-phenolsulfonate buffers without sodium chloride are given. Estimation of the ionic strength of a mixture of potassium *p*-phenolsulfonate and sodium hydroxide from the change in emf which results on the addition of sodium chloride to the buffer and application of the method to unknowns are discussed.

II. EXPERIMENTAL PROCEDURE AND THE CALCULATION OF pH

The purification and analysis of potassium *p*-phenolsulfonate and sodium chloride, the preparation and standardization of a carbonate-free solution of sodium hydroxide, the preparation of the buffer solutions from these materials and conductivity water in an atmosphere freed of carbon dioxide, and other details of the experimental technique have been described [1, 6].

The emf values given in table 1 have been corrected in the usual way to a partial pressure of hydrogen of 760 mm. The four solutions [2]

[2] The buffers of series A are, respectively, solutions A1, A2, A4, and A6 prepared in the earlier study of phenolsulfonate-chloride mixtures [1]. As before, HPs will be written for the univalent phenolsulfonate anion, $HOC_6H_4SO_3^-$, and Ps for the bivalent phenolate-sulfonate anion, $OC_6H_4SO_3^=$.

of series A contain approximately the same molal concentration of sodium chloride, m_3, as of potassium *p*-phenolsulfonate (KHPs), m_1, and of potassium sodium *p*-phenolatesulfonate (KNaPs), m_2, whereas series B, C, and D comprise solutions which have, respectively, one-half, one-quarter, and one-tenth as much sodium chloride as buffer salt. The molalities of each constituent are given in columns 2, 3, and 4 of table 1.

TABLE 1.—*Electromotive forces of hydrogen–silver-chloride cells containing mixtures of potassium p-phenolsulfonate (m_1), potassium sodium p-phenolate sulfonate (m_2), and sodium chloride (m_3)*

Solution number	m_1	m_2	m_3	$E_0°$	$E_5°$	$E_{10}°$	$E_{15}°$	$E_{20}°$
A1	0.09628	0.09744	0.09622	0.78744	0.79105	0.79460	0.79807	0.80156
A2	.05979	.06051	.05975	.79900	.80295	.80674	.81048	.81418
A3	.03070	.03107	.03068	.81578	.82003	.82419	.82830	.83235
A4	.009425	.009539	.009419	.84605	.85091	.85570	.86040	.86502
B1	.10376	.09751	.04951	.80171	.80555	.80928	.81302	.81672
B2	.04853	.04561	.02316	.82037	.82464	.82883	.83294	.83705
B3	.017932	.016851	.008556	.84581	.85057	.85521	.85989	.86451
C1	.09736	.09753	.02549	.81894	.82308	.82714	.83117	.83520
C2	.04058	.04065	.010626	.84046	.84513	.84969	.85417	.85868
D1	.09736	.09753	.010051	.84090	.84545	.84991	.85434	.85876
D2	.04594	.04682	.004743	.85945	.86440	.86929	.87410	.87893
D3	.019838	.019872	.002048	.88062	.88601	.89130	.89658	.90190
	$E_{25}°$	$E_{30}°$	$E_{35}°$	$E_{40}°$	$E_{45}°$	$E_{50}°$	$E_{55}°$	$E_{60}°$
A1	0.80500	0.80839	0.81160	0.81506	0.81833	0.82159	0.82482	0.82808
A2	.81793	.82157	.82517	.82878	.83229	.83583	.83930	.84278
A3	.83644	.84046	.84441	.84839	.85224	.85613	.85993	.86376
A4	.86979	.87434	.87888	.88343	.88789	.89234	.89664	.90104
B1	.82042	.82404	.82764	.83120	.83475	.83827	.84175	.84524
B2	.84116	.84525	.84916	.85317	.85708	.86097	.86485	.86874
B3	.86923	.87385	.87824	.88278	.88717	.89164	.89599	.90015
C1	.83926	.84323	.84709	.85102	.85489	.85875	.86255	.86636
C2	.86321	.86770	.87200	.87642	.88074	.88507	.88935	.89361
D1	.86322	.86761	.87179	.87611	.88040	.88462	.88885	.89303
D2	.88376	.88858	.89319	.89789	.90259	.90721	.91175	.91626
D3	.90730	.91251	.91748	.92233	.92770	.93262	.93752	.94228

The pH values of the mixtures of *p*-phenolsulfonate, *p*-phenolate sulfonate, and chloride salts can be computed readily from the equation[3]

$$\mathrm{pH}=(E-E°)/k+\log m_{\mathrm{Cl}}-A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})+\beta\mu, \qquad (1)$$

provided that the parameters a_i and β have been determined. It is possible to find the necessary values of a_i from the change of the next to the last term of eq 1 with ionic strength. This change is observed most simply by plotting pK_2', the negative of the common logarithm of the "apparent" second dissociation constant of phenolsulfonic acid, as a function of ionic strength, where pK_2' is given by

$$pK_2'=(E-E°)/k+\log\,(m_{\mathrm{HPs}}m_{\mathrm{Cl}}/m_{\mathrm{Ps}})+2A\sqrt{\mu}/(1+Ba_i\sqrt{\mu}). \qquad (2)$$

[1] E and $E°$ represent the emf and standard potential of the cell which contains hydrogen and silver chloride electrodes, and k is $2.3026RT/F$. A and B are constants of the Debye-Hückel equation. A recalculation of A, B, and k was recently reported [7]. No change was made in the value of k between 0° and 50° C, and $E°$ therefore remains unaltered. A new extrapolation curve computed from the emf data of Harned and Ehlers [8] (from which $E°$ is derived) would, however, show a slightly different slope, as a result of the small changes that were made in the values of A and B.

The ionic strength, μ, is given by $m_1+3m_2+m_3-m_{\mathrm{OH}}$. The calculation of m_{OH} from the dissociation constants of water and of the phenol group was made as described in the earlier paper [1].

The proper value of a_i gives a straight-line plot of pK_2' with respect to ionic strength. This straight line extrapolates to pK_2, the negative of the common logarithm of the thermodynamic dissociation constant, at an ionic strength of zero. Since pK_2' and pK_2 are then both known, β is readily obtained from the equation

$$\beta=(pK_2-pK_2')/\mu. \qquad (3)$$

A value of 8.0 A for a_i was found to yield pK_2' values that varied linearly with ionic strength for each series of solutions at all 13 temperatures. Extrapolation of these lines to zero ionic strength yielded, within the error of the experiments, the same values of pK_2 as were obtained in the detailed study of 39 solutions with 2 different buffer ratios [1].

The plots of pK_2' as a function of ionic strength for the four series of buffers at 0°, 25°, and 60° C are shown in figure 1. A correction for hydrolysis was made [1]. The values of $3A$, $8B$, and β are listed in table 2.

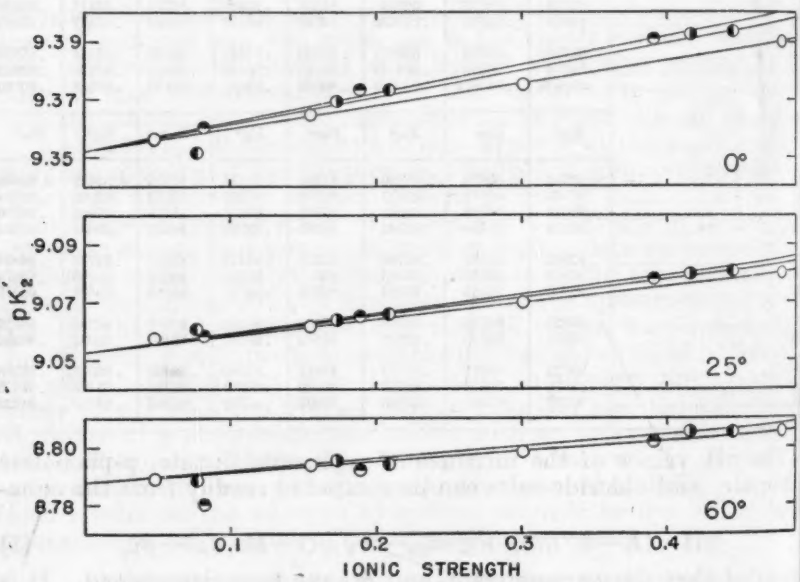

FIGURE 1.—*Plot of pK_2' (eq 2) as a function of ionic strength at 0°, 25°, and 60° C.*

○=series A; ◐=series B; ◑=series C; ◓=series D

TABLE 2.—*Numerical values of 3A, 8B, and β from 0° to 60° C*

t	$3A$	$8B$	$-\beta$ for series		
			A	B	C and D
°C					
0	1.467	2.602	0.079	0.094	0.100
5	1.478	2.609	.075	.087	.092
10	1.490	2.616	.069	.077	.082
15	1.503	2.623	.066	.074	.078
20	1.516	2.631	.061	.069	.071
25	1.529	2.638	.057	.063	.066
30	1.544	2.647	.052	.057	.061
35	1.559	2.656	.049	.053	.053
40	1.575	2.664	.046	.051	.051
45	1.591	2.674	.042	.047	.047
50	1.607	2.682	.040	.045	.045
55	1.625	2.693	.040	.045	.045
60	1.643	2.702	.038	.043	.043

The pH of each mixture is given in table 3. These values were computed from eq 1 with the use of 8.0 A for a_i and the values of β given in table 2. The error in establishing a_i is estimated to be about ±0.2 A, and the uncertainty in pH from this source is somewhat less than 0.002 unit.

TABLE 3.—pH *values of mixtures of potassium p-phenolsulfonate* (m_1), *potassium sodium p-phenolate sulfonate* (m_2), *and sodium chloride* (m_3)

Solution number	m_1	m_2	m_3	pH at—				
				0°	5°	10°	15°	20°
A1	0.09628	0.09744	0.09622	8.992	8.923	8.857	8.795	8.738
A2	.05979	.06051	.05975	9.024	8.956	8.889	8.828	8.770
A3	.03070	.03107	.03068	9.072	9.003	8.937	8.876	8.818
A4	.009425	.009539	.009419	9.154	9.085	9.025	8.959	8.901
B1	.10376	.09751	.04951	8.967	8.897	8.831	8.769	8.711
B2	.04853	.04561	.02316	9.022	8.951	8.885	8.823	8.765
B3	.017932	.016851	.008556	9.093	9.023	8.955	8.890	8.837
C1	.09736	.09753	.02549	8.998	8.928	8.862	8.800	8.743
C2	.04058	.04065	.010626	9.059	8.990	8.924	8.861	8.805
D1	.09736	.09753	.010051	9.004	8.933	8.867	8.805	8.747
D2	.04594	.04682	.04743	9.056	8.986	8.920	8.856	8.800
D3	.019838	.019872	.002048	9.113	9.042	8.976	8.914	8.857

Solution number	pH at—							
	25°	30°	35°	40°	45°	50°	55°	60°
A1	8.682	8.633	8.585	8.542	8.502	8.464	8.427	8.395
A2	8.715	8.665	8.618	8.575	8.535	8.498	8.461	8.429
A3	8.763	8.713	8.667	8.624	8.584	8.547	8.511	8.479
A4	8.848	8.797	8.751	8.709	8.669	8.632	8.595	8.564
B1	8.656	8.606	8.559	8.514	8.475	8.437	8.400	8.368
B2	8.709	8.660	8.612	8.568	8.527	8.490	8.454	8.422
B3	8.783	8.735	8.686	8.643	8.601	8.567	8.531	8.495
C1	8.689	8.638	8.591	8.547	8.509	8.470	8.433	8.401
C2	8.750	8.700	8.653	8.609	8.570	8.533	8.498	8.466
D1	8.692	8.642	8.594	8.550	8.511	8.472	8.436	8.404
D2	8.744	8.694	8.647	8.602	8.564	8.527	8.490	8.456
D3	8.804	8.754	8.706	8.658	8.621	8.582	8.546	8.510

III. EQUATIONS FOR THE SALT EFFECT

The negative of the logarithm of the mean activity coefficient of hydrochloric acid ($f_{\pm}=\sqrt{f_{H}f_{Cl}}$) in each series of *p*-phenolsulfonate-chloride mixtures is expressed by

$$-\log f_{\pm}=\frac{A\sqrt{\mu}}{1+8B\sqrt{\mu}}-\beta\mu, \tag{4}$$

where f represents the activity coefficient on the molal scale. The first term on the right of eq 4 has been found to remain unaltered by a change in molal ratio of chloride to *p*-phenolsulfonate, at constant ionic strength. Under these conditions, then, the change in activity coefficient of hydrochloric acid is described completely by the change in β. Furthermore, this situation may be assumed to persist in the limit of pure buffer, that is, when a negligible concentration of sodium chloride remains. If the mean activity coefficient of hydrochloric acid in the absence of sodium chloride is $f^{\circ}_{\pm}$, and the corresponding limit of β is β°, it follows that

$$\log f_{\pm}=\log f^{\circ}_{\pm}+(\beta-\beta^{\circ})\mu, \tag{5}$$

for any given ionic strength. Within the estimated error of 0.002, β varies linearly with the fractional contribution of chloride ion to the total ionic strength of the mixture, $m_3/2\mu=r$. If, then, $\beta-\beta^{\circ}=\alpha' r$, we have, from eq 5,

$$\log(f_{\pm}/f^{\circ}_{\pm})=\alpha' r\mu=\alpha m_3, \tag{6}$$

where $\alpha'=2\alpha$. The "activity deviations", $\log(f_{\pm}/f^{\circ}_{\pm})$, of these mixtures are, therefore, a linear function of the molality of sodium chloride at constant total ionic strength. Equation 6 is similar in form to equations that express the linear variation of the logarithm of the activity coefficient of hydrochloric acid with molality of acid in chloride mixtures of constant ionic strength, as found by Harned [9] and by Güntelberg [10].[4]

For the solutions considered here, r varies between 0.01 and 0.1. At 25° C, α' is found to be 0.106. The activity deviations have been computed from eq 6 for four values of r at four ionic strengths. These deviations are given in table 4.

Since the changing ratio of chloride to *p*-phenolsulfonate in the four series of solutions appears not to effect a corresponding change in a_{H}, the pH values of all of these mixtures can be computed from a single equation, derived from the law of mass action:

$$\mathrm{pH}=\mathrm{p}K_2-\log(m_{\mathrm{HPs}}/m_{\mathrm{Ps}})-3A\sqrt{\mu}/(1+8B\sqrt{\mu}). \tag{7}$$

It is evident, therefore, that the effect of salt on the pH values of

[4] The linear variation is a consequence of the principle of specific or abnormal salt effects discussed by Acree [11] and coworkers, or specific ionic interaction, as stated by Brönsted [12]. The original Brönsted formulation split the activity coefficient of an ion in a mixture of two electrolytes in dilute aqueous solution into the product of "interaction coefficients" and "salting-out coefficients." Only first-order interactions were considered, and it was assumed that ions are uniformly influenced by ions of like charge as a result of the strong repulsive forces between them. Scatchard and Prentiss [13] extended Brönsted's treatment to include ionic interactions of higher orders. Their experimental work offers extensive confirmation of the basic postulates of the theory. If higher terms are taken into account, the individual thermodynamic properties need no longer vary linearly with composition, although the departure from linearity is small. Small deviations from the results predicted by the theory may, however, indicate the necessity of considering specific effects between ions of like sign, as Harned [9] has shown.

TABLE 4.—*Activity deviations in mixtures of constant total ionic strength at 25° C computed from eq 6*

[$f_{\pm}/f^{\circ}_{\pm}$ is the ratio of the mean activity coefficient of hydrochloric acid in a mixture of phenolsulfonate buffer and sodium chloride to the activity coefficient in the pure buffer at the same ionic strength. r is the fractional contribution of chloride ion to the ionic strength. a' is 0.106 at 25° C.]

r	$\log (f_{\pm}/f^{\circ}_{\pm})$	r	$\log (f_{\pm}/f^{\circ}_{\pm})$
μ=0.05		μ=0.25	
0.01	0.0001	0.01	0.0003
.025	.0001	.025	.0007
.05	.0003	.05	.0013
.10	.0005	.10	.0027
μ=0.10		μ=0.50	
0.01	0.0001	0.01	0.0005
.025	.0003	.025	.0013
.05	.0005	.05	.0027
.10	.0011	.10	.0053

these buffers in the range of concentrations studied in this investigation is satisfactorily accounted for solely by the change in ionic strength (and activity coefficients) attendant upon the addition of a third ionized component to the buffer. Abnormal or specific effects of the sodium and chloride ions appear to be absent. The pH of a mixture that contains sodium chloride is, therefore, the same as that of a more concentrated buffer of the same ionic strength and buffer ratio to which no salt has been added. This type of behavior might well be termed the *normal salt effect*. On the other hand, a change of a_t (and of pH) with a change of the ratio of sodium chloride to buffer at constant ionic strength would seem to indicate abnormal or specific interactions among the ions.

Equations of the form of eq 7 can be combined by subtraction to represent the pH of a buffer that contains sodium chloride in terms of the value, pH°, for the same buffer in the absence of sodium chloride. Since the first two terms on the right of eq 7 do not change with addition of salt,[5] the following expression is obtained:

$$\mathrm{pH}=\mathrm{pH}^{\circ}-3A\left[\frac{\sqrt{\mu^{\circ}+m}}{1+8B\sqrt{\mu^{\circ}+m}}-\frac{\sqrt{\mu^{\circ}}}{1+8B\sqrt{\mu^{\circ}}}\right]=\mathrm{pH}^{\circ}-3A\phi(m), \quad (8)$$

where μ° is the ionic strength of the buffer without sodium chloride, m is the molality of sodium chloride, and $\phi\,(m)$ represents that part of eq 8 inclosed in brackets.

The quantity $\phi(m)$ was evaluated for six buffer solutions in which the molalities of *p*-phenolsulfonate and *p*-phenolate-sulfonate ions were both 0.01, 0.02, 0.04, 0.05, 0.075, and 0.1. Plots of $\phi(m)$ with respect to m suggested that $\phi(m)$ could be represented satisfactorily by $am+bm^2$. The numerical values of a and b were then obtained by the method of least squares and are given in table 5. The following equation permits a calculation of the pH values of these six buffers from 0° to 60° C with a mean deviation of less than 0.001 unit when the

[5] The salt effect on the hydrolysis of the $Ps^{=}$ ion is so small at all temperatures from 0° to 60° C that the second term on the right of eq 7 is altered by less than 0.001 pH unit by the addition of 0.1 mole of sodium chloride to a liter of any buffer more concentrated than 0.01 *m*.

molality of sodium chloride, m, is equal to, or less than, the molality of the buffer:

$$pH = pH° - 3A(am + bm^2). \quad (9)$$

The values of $3A$ are given in table 2, and pH° is found in table 6. The change of pH of the six buffer solutions at 25° C with concentration of sodium chloride is shown in figure 2.[6]

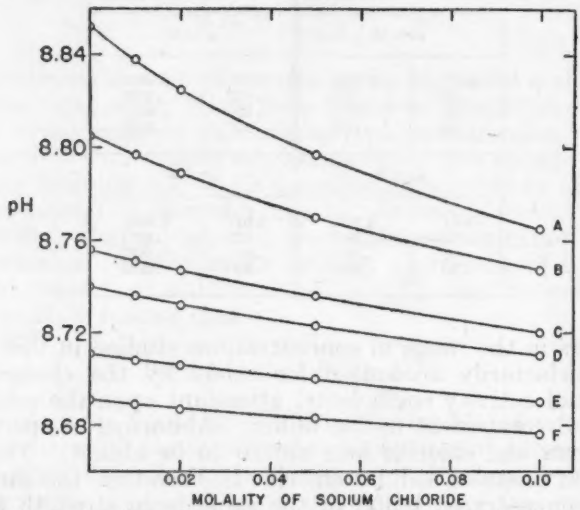

FIGURE 2.—*Effect of sodium chloride on the* pH *values of six phenolsulfonate buffers at 25° C.*

Curves A, B, C, D, E, and F represent 0.01, 0.02, 0.04. 0.05, 0.075, and 0.1 molal buffers, respectively.

TABLE 5.—*Constants of equation 9*

Molality of buffer	a	$-b$	Molality of buffer	a	$-b$
0.01	0.961	4.00	0.05	0.243	0.53
.02	.554	1.75	.075	.167	.38
.04	.306	0.78	.1	.100	.00

IV. STANDARD BUFFER SOLUTIONS

The pH values, pH°, of potassium p-phenolsulfonate solutions in which the phenol group is half neutralized with sodium hydroxide and which contain no sodium chloride are listed in table 6 for 13 temperatures from 0° to 60° C. These values were calculated by eq 7 with the use of the second dissociation constant of p-phenolsulfonic acid as determined earlier by Bates, Siegel, and Acree [1] and confirmed by the measurements reported in this paper. The compositions of the six buffer solutions are given in table 7. The approximate specific gravities required for the computation of the total volumes of the solutions were estimated from the values for solutions of potassium sulfate and of potassium tartrate. The change of pH with temperature for four of these buffers without sodium chloride is shown in figure 3.

[6] There is no justification from these experiments for the use of eq 7 and 9 for the calculation of the pH of a buffer-chloride mixture in which the molality of sodium chloride exceeds that of the buffer. It is likely, however, that the linear relationship of eq 6 is valid at somewhat higher values of r than those actually used. These equations have accordingly been employed to compute the pH for molalities of sodium chloride up to one-tenth, as shown in figure 2.

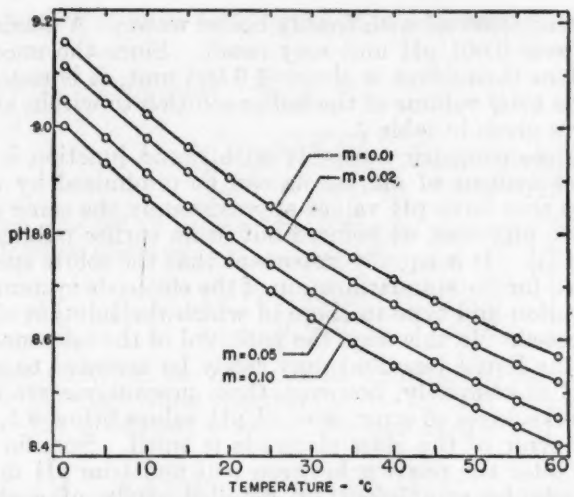

FIGURE 3.—pH *of four phenolsulfonate buffers plotted as a function of temperature.*
The buffer ratio is unity in each case, and *m* is the molality of potassium *p*-phenolsulfonate and of potassium sodium *p*-phenolate sulfonate.

TABLE 6.—pH *values of six phenolsulfonate buffers without sodium chloride from 0° to 60° C*

t	pH° for—					
	0.01 *m* buffer	0.02 *m* buffer	0.04 *m* buffer	0.05 *m* buffer	0.075 *m* buffer	0.1 *m* buffer
°C						
0	9.159	9.113	9.064	9.049	9.021	9.001
5	9.089	9.044	8.995	8.979	8.951	8.931
10	9.024	8.978	8.929	8.913	8.885	8.865
15	8.962	8.916	8.867	8.851	8.823	8.803
20	8.905	8.859	8.810	8.794	8.765	8.745
25	8.852	8.805	8.756	8.740	8.711	8.691
30	8.802	8.755	8.705	8.689	8.660	8.640
35	8.755	8.708	8.659	8.643	8.613	8.593
40	8.713	8.666	8.616	8.600	8.570	8.550
45	8.673	8.626	8.575	8.558	8.529	8.509
50	8.637	8.588	8.538	8.521	8.492	8.472
55	8.601	8.553	8.502	8.485	8.455	8.436
60	8.569	8.521	8.470	8.453	8.423	8.402

TABLE 7.—*Compositions of six buffer standards of potassium* p-*phenolsulfonate and sodium hydroxide*

Molality of buffer	Potassium *p*-phenolsulfonate	Sodium hydroxide	Total volume of solution
	g	*Moles*	*ml*
0.01	4.245	0.01	1,002
.02	8.490	.02	1,005
.04	16.980	.04	1,008
.05	21.23	.05	1,010
.075	31.84	.075	1,012
.1	42.45	.1	1,015

These buffers can be prepared conveniently by dissolving the specified weights of pure potassium *p*-phenolsulfonate in the proper volume of a carbonate-free solution of sodium hydroxide and diluting

to a volume of 1,000 ml with freshly boiled water. A maximum error of slightly over 0.001 pH unit may result. Since the uncertainty in the pH values themselves is about ± 0.003 unit, it is necessary only to adjust the total volume of the buffer solution to within about 20 ml of the figures given in table 7.

When an electrometric assembly with liquid junction is employed for the measurement of pH, errors can be minimized by calibration with buffers that have pH values approximately the same as those of the unknown mixtures, as pointed out in an earlier publication from this Bureau [3]. It is equally important that the solute species in the buffer chosen for the standardization of the electrode system be similar in concentration and type to those of which the solution of unknown pH is composed. In this way, the potential of the reference electrode (including the liquid junction) may safely be assumed to remain unchanged. Unfortunately, however, these precautions are insufficient to remove all sources of error, even at pH values below 9.5, where the sodium-ion error of the glass electrode is small. Specific properties of the ions alter the relation between emf and true pH in a manner that can only be established by detailed study of each solution. Measurements made in this way will accordingly be subject to residual uncertainties of 0.01 to 0.05 pH unit.

It is suggested that *p*-phenolsulfonate buffers be used as standards for the calibration of pH equipment to be used in the range pH 8.0 to 9.0. Phosphate buffers that have a pH of about 7.0 [6] can be used for unknowns up to pH 8.0, and borax solutions (pH about 9.2 [3, 14]) can be employed successfully in the upper range of the phenolsulfonate buffers and above. When the approximate total ion concentration of the unknown solution can be estimated, the accuracy of the pH measurement can be increased somewhat by use of a standard buffer of approximately the same ionic strength.

V. ESTIMATION OF THE IONIC STRENGTH AND pH OF UNKNOWN MIXTURES OF POTASSIUM *p*-PHENOLSULFONATE AND SODIUM HYDROXIDE

With the use of eq 9 and the constants a and b given in table 5 it can be shown that the pH of the 0.01 m buffer is altered about six times as much as that of the 0.1 m buffer upon the addition of a given molal increment of sodium chloride. This dependence of the salt effect on the ionic strength of the buffer suggests the possibility of estimating the ionic strengths and pH values of mixtures of potassium *p*-phenolsulfonate and sodium hydroxide of unknown composition from the change of emf which results from the addition of sodium chloride.

If sodium chloride is added to two portions of the unknown buffer in such amounts that the molality of this salt in solution 1 is m_{Cl} and that in solution 2 is $m_{Cl}+\Delta m$, and these two solutions are made the electrolytes of cells which contain hydrogen and silver chloride electrodes, the pH values of the solutions are given by

$$pH_1=(E_1-E^\circ)/k+\log m_{Cl}-A\sqrt{\mu_1}/(1+8B\sqrt{\mu_1})+\beta\mu_1, \quad (10)$$

and

$$pH_2=(E_2-E^\circ)/k+\log (m_{Cl}+\Delta m)-A\sqrt{\mu_1+\Delta m}/(1+8B\sqrt{\mu_1+\Delta m}) +\beta(\mu_1+\Delta m). \quad (11)$$

Subtraction of eq 11 from eq 10 gives an expression for the difference of pH:

$$pH_1-pH_2=(E_1-E_2)/k+\log\frac{m_{Cl}}{m_{Cl}+\Delta m}+$$

$$A\left[\frac{\sqrt{\mu_1+\Delta m}}{1+8B\sqrt{\mu_1+\Delta m}}-\frac{\sqrt{\mu_1}}{1+8B\sqrt{\mu_1}}\right]-\beta\Delta m. \quad (12)$$

Furthermore, the pH of each solution can be expressed by eq 7, and the pH difference becomes

$$pH_1-pH_2=3A\left[\frac{\sqrt{\mu_1+\Delta m}}{1+8B\sqrt{\mu_1+\Delta m}}-\frac{\sqrt{\mu_1}}{1+8B\sqrt{\mu_1}}\right], \quad (13)$$

since the salt effect on the buffer ratio is negligible (see footnote 5).

Equating the right-hand members of eq 12 and 13 yields an expression for the difference between the emf of the two cells:

$$(E_1-E_2)/k=2A\left[\frac{\sqrt{\mu_1+\Delta m}}{1+8B\sqrt{\mu_1+\Delta m}}-\frac{\sqrt{\mu_1}}{1+8B\sqrt{\mu_1}}\right]+\beta\Delta m-\log\frac{m_{Cl}}{m_{Cl}+\Delta m}$$

$$=2A\phi(\Delta m)+\beta\Delta m-\log\frac{m_{Cl}}{m_{Cl}+\Delta m}, \quad (14)$$

where ϕ (Δm) represents the quantity in brackets in eq 12, 13, and 14.

The difference between the emf of the two cells which contain the same buffer but different amounts of sodium chloride can be computed from eq 14 for values of μ_1, the ionic strength of the more dilute solution, between 0 and 0.5, the probable limits of validity of the equations for pH. When the approximate value of μ_1 has been ascertained, the approximate pH of the solution more dilute in chloride can be computed. For simplicity, eq 10 can be rewritten

$$pH_1=(E_1-E^\circ)/k+\phi(\mu_1), \quad (15)$$

where

$$\phi(\mu_1)=\log m_{Cl}-\frac{A\sqrt{\mu_1}}{1+8B\sqrt{\mu_1}}+\beta\mu_1. \quad (16)$$

The "total salt error," the error in pH which results from considering all activity coefficients equal to unity, is thus $\phi(\mu_1)-\log m_{Cl}$. A mean value of -0.06 can be employed for β at 25° C. Changes of buffer ratio and ratio of sodium chloride to buffer do not alter the value of a_i and are without marked influence upon β, as may be seen in table 2 of this paper and table 3 of the paper by Bates, Siegel, and Acree [1].

With the use of eq 14 and 16, calculations of E_1-E_2 and $\phi(\mu_1)$ at 25° C have been made for values of μ_1 from 0.02 to 0.50 when $m_{Cl}=0.01$, $\Delta m=0.09$, and $\beta=-0.06$. The results are given in table 8. The conditions for the use of table 8 are met when the molalities of sodium chloride in solutions 1 and 2 are 0.01 and 0.1. The ionic strength of the original mixture is, then, $\mu_1-0.01$. The weights of sodium chloride which correspond to these molalities are, respectively, 0.5845 g and 5.845 g for each 1,000 g of solvent. Chloride ion must obviously be absent from the original buffer mixture or, if present

to the extent of not more than 0.01 mole per liter, its concentration determined and the necessary corrections applied to the quantity of salt added.

TABLE 8.—*Values of E_1-E_2 and $\phi(\mu_1)$ at 25° C computed from eq 14 and 16 for various values of μ_1*

[$m_{Cl}=0.01$; $\Delta m=0.09$; $\beta=-0.06$]

μ_1	E_1-E_2	$^a\phi(\mu_1)$	μ_1	E_1-E_2	$^a\phi(\mu_1)$	μ_1	E_1-E_2	$^a\phi(\mu_1)$
	mv			*mv*			*mv*	
0.02	63.28	−2.047	0.22	59.79	−2.113	0.42	59.38	−2.140
.04	62.10	−2.062	.24	59.67	−2.116	.44	59.32	−2.142
.06	61.45	−2.073	.26	59.67	−2.120	.46	59.32	−2.145
.08	60.97	−2.081	.28	59.61	−2.123	.48	59.26	−2.147
.10	60.74	−2.087	.30	59.55	−2.125	.50	59.26	−2.149
.12	60.44	−2.092	.32	59.49	−2.128			
.14	60.26	−2.097	.34	59.44	−2.130			
.16	60.09	−2.102	.36	59.44	−2.133			
.18	59.97	−2.106	.38	59.38	−2.136			
.20	59.85	−2.110	.40	59.38	−2.138			

[a] The hydrogen-pressure correction to E_1 has been made by the addition of 0.007 to each of the values of $\phi(\mu_1)$ computed from eq 16.
The "total salt error" for each solution of ionic strength μ_1 is given by $\phi(\mu_1)+2$ (see eq 16).

In eq 10 and 11, E represents the emf of the cell corrected as usual to a partial pressure of hydrogen of 760 mm. The normal barometric pressure in many laboratories is in the vicinity of 760 mm, and the correction to the emf therefore corresponds, for dilute solutions, to an increase of 0.007 unit in pH at 25° C. The values of $\phi(\mu_1)$ listed in table 8 include this correction to the pH, and it is intended that the value of E_1 used in eq 15 shall be the uncorrected emf. An error of not more than 0.006 in pH will result if the barometric pressure is between 740 and 780 mm. A pressure correction is, of course, unnecessary to obtain the difference of emf, E_1-E_2, if the two cells are measured at the same barometric pressure.

When it is desired to obtain by this method the approximate pH of a solution containing unknown quantities of potassium *p*-phenolsulfonate and sodium hydroxide, sodium chloride is added to two portions of the buffer in amounts which correspond to 0.01 and 0.1 mole per liter of buffer. The potentials between hydrogen and silver chloride electrodes in cells which contain the two buffer-chloride mixtures are measured at 25° C. The difference of emf is obtained and $\phi(\mu_1)$ found from table 8. The pH of the more dilute chloride solution (solution 1) is then computed from eq 15. The values of E° and k are, respectively, 0.2224 and 0.05914. The pH of the original buffer is slightly higher than that of solution 1, but the difference is less than 0.014 unit if the buffer concentration is greater than 0.01.

The substitution of molarity of chloride ion for molality, if necessary, need cause little concern, if an estimate of the ionic strength alone is desired. In order that the last term of eq 14 shall remain equal to 1, it is necessary only to add 0.01 mole and 0.1 mole of sodium chloride to equal *volumes* of the buffer solution. If this procedure is followed, Δm is no longer exactly 0.09. Changes that amount to less than 5 percent of Δm, however, do not appreciably alter the emf differences listed in table 8. On the other hand, the pH of solution 1 computed from eq 10 may be too low by more than 0.01 unit, if the concentration of chloride ion on the molar scale is used instead of the molality. When 0.01 mole of sodium chloride is added to a liter of

0.1 *m* phenolsulfonate buffer, the concentration of chloride on the molar scale is from 4 to 5 percent lower than the molality, and an error of about 0.02 pH unit will result. As the buffer concentration is lowered, the difference between the concentrations of chloride ion on the weight and volume scales, and consequently the error in pH, will be reduced.

Only a rough estimate of the ionic strength is obtainable by the method outlined here, for the differences of emf, as shown in table 8, are insensitive to small changes of ionic strength when the buffer concentration is high. Fortunately, the corresponding changes of $\phi(\mu_1)$ and of pH are small in this region, and an accurate estimate of ionic strength is unnecessary for the calculation of pH at high concentrations by eq 15. The table also shows, however, that the pH value computed from eq 10 and 15 could be in error by 0.1 unit or more, if the contribution of the buffer to the total ionic strength were ignored completely. The "total salt error" must be carefully considered in dealing with unknowns. Tables similar to table 8 can be constructed for other buffer systems when the values of a_t and β are available. This procedure should find application whenever it is desired to ascertain the approximate ionic strengths of buffer mixtures which vary in concentration but not in type.

VI. REFERENCES

[1] R. G. Bates, G. L. Siegel, and S. F. Acree, J. Research NBS **31,** 205 (1943) RP1559.
[2] E. E. Sager, M. R. Schooley, and S. F. Acree, J. Research NBS **31,** 197 (1943) RP1558.
[3] R. G. Bates, W. J. Hamer, G. G. Manov, and S. F. Acree, J. Research NBS **29,** 183 (1942) RP1495.
[4] B. Wingfield and S. F. Acree, J. Research NBS **27,** 361 (1941) RP1424.
[5] E. E. Sager, H. J. Keegan, and S. F. Acree, J. Research NBS **31,** 323 (1943) RP1569.
[6] R. G. Bates and S. F. Acree, J. Research NBS **30,** 129 (1943) RP1524.
[7] G. G. Manov, R. G. Bates, W. J. Hamer, and S. F. Acree, J. Am. Chem. Soc. **65,** 1765 (1943).
[8] H. S. Harned and R. W. Ehlers, J. Am. Chem. Soc. **55,** 2179 (1933).
[9] H. S. Harned, J. Am. Chem. Soc. **48,** 326 (1926); **57,** 1865 (1935).
[10] E. Güntelberg, Z. physik. Chem. **123,** 199 (1926).
[11] S. F. Acree and associates, Am. Chem. J. **38,** 1 (1907); **39,** 528 (1908); **41,** 483 (1909); **42,** 130 (1909); **48,** 372 (1912); **49,** 347, 379, 485 (1913). J. Am. Chem. Soc. **38,** 2148, 2156, 2772 (1916); **39,** 386 (1917). Ber. deut. chem. Ges. **41,** 3219 (1908). J. Bact. **5,** 169 (1920). J. Research NBS **27,** 362 (1941) RP1424; **31,** 323 (1943) RP1569. N. E. Loomis, J. L. Essex, and M. R. Meacham, J. Am. Chem. Soc. **39,** 1133 (1917).
[12] J. N. Brönsted, J. Am. Chem. Soc. **44,** 877 (1922); **45,** 2898 (1923).
[13] G. Scatchard and S. S. Prentiss, J. Am. Chem. Soc. **56,** 2320 (1934).
[14] D. I. Hitchcock and A. C. Taylor, J. Am. Chem. Soc. **59,** 1812 (1937); **60,** 2710 (1938).

WASHINGTON, February 5, 1944.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1581

Part of Journal of Research of the National Bureau of Standards, Volume 32, April 1944

THERMAL EXPANSION OF HIGH-SILICON CAST IRON

By Peter Hidnert and George Dickson

ABSTRACT

This paper gives data on the linear thermal expansion of high-silicon cast iron containing approximately 14 percent of silicon, with 3 percent of molybdenum and without appreciable molybdenum, at various temperatures between 20° and 700° C. Differences between the coefficients of expansion of these high-silicon cast irons were found to be slight. Both high-silicon cast irons were found to have slightly higher coefficients of expansion than electrolytic iron for temperature ranges between 20° and 300° C, and appreciably higher coefficients for higher temperature ranges. No indication of growth similar to that of ordinary cast iron was observed on heating the high-silicon cast iron to 700° C.

CONTENTS

	Page
I. Introduction	145
II. Material investigated	146
III. Apparatus	146
IV. Results and discussion	146
V. References	149

I. INTRODUCTION

In 1938, discordant values (0.7×10^{-5} and 0.36×10^{-5} per degree Fahrenheit between 32° and 212° F) were reported by manufacturers [1] for the coefficient of linear thermal expansion of high-silicon cast iron containing 14.5 percent of silicon. The lower value was also reported [1] [1] for a 14.5-percent silicon cast iron containing 3 percent of molybdenum. The work reported in the present paper was undertaken in order to determine definitely the coefficients of expansion of high-silicon cast iron with 3 percent of molybdenum and without appreciable molybdenum, for various temperature ranges between 20° and 700° C.

Some of the uses of high-silicon cast iron are indicated in an anonymous paper [2] and in a book by Greiner, Marsh, and Stoughton [3]. For example, high-silicon cast iron is used where resistance to hot concentrated sulfuric acid, copper sulfate solutions, or tin tetrachloride is required.

High-silicon cast iron containing usually 14 to 16 percent of silicon and 1 percent or less of carbon is known [1, 3] by a variety of trade names, such as Antaciron, Durichlor, Duriron, Elianite, Fersilite, Ironac, Métillure, Tantiron, and Thermsilid.

[1] Numbers in brackets indicate the literature references at the end of this paper.

II. MATERIAL INVESTIGATED

Two annealed high-silicon cast irons obtained from the Duriron Co., Inc., Dayton, Ohio, were used in this investigation. Table 1 gives the chemical composition of the samples. The diameter of sample 1678 was 11 mm, and the cross section of sample 1679 was 8 by 8 mm. Each sample was ground to a length of 300 mm with the ends cylindrical (radius 150 mm). The samples could not be machined on account of their brittleness.

III. APPARATUS

The precision micrometric thermal-expansion apparatus described by Souder and Hidnert [4] was used for the determinations of linear thermal expansion. Figure 4 of their publication indicates the method used in mounting the samples in the furnace. A platinum-osmium (about 6½ percent of osmium) observation wire 0.002 inch in diameter was in contact with each end of the sample.

IV. RESULTS AND DISCUSSION

Figures 1 and 2 show the observations on the linear thermal expansion of the two high-silicon cast irons at various temperatures between

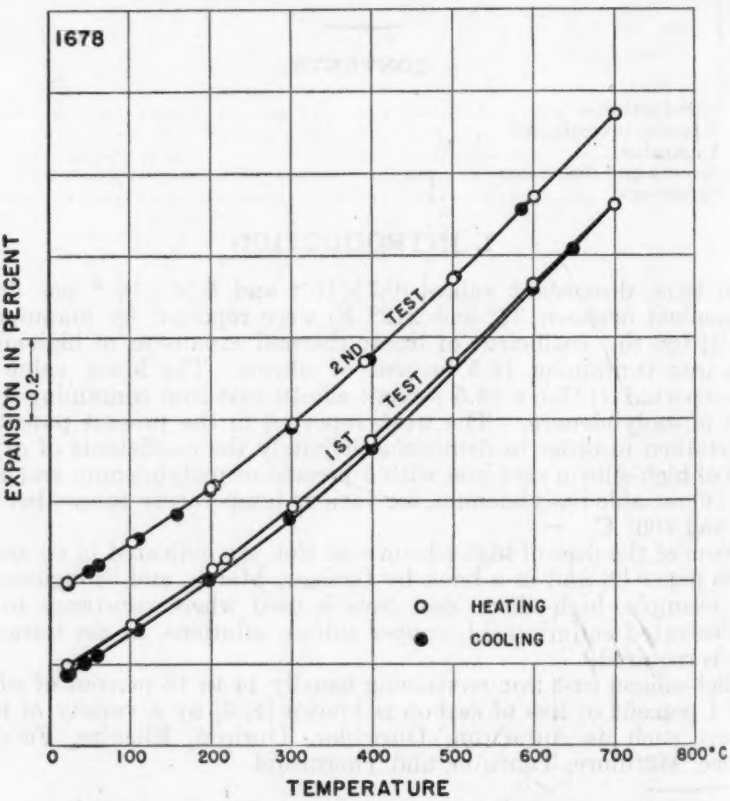

FIGURE 1.—*Linear thermal expansion of high-silicon cast iron.*

Si, 14.7; Mn, 0.75; C, 0.41; S, 0.015; P, 0.023; Mo, 0.05 percent.

20° and 700° C. In the first test of each cast iron, there was a divergence between the expansion and the contraction curve, but in the second test these curves nearly coincided.

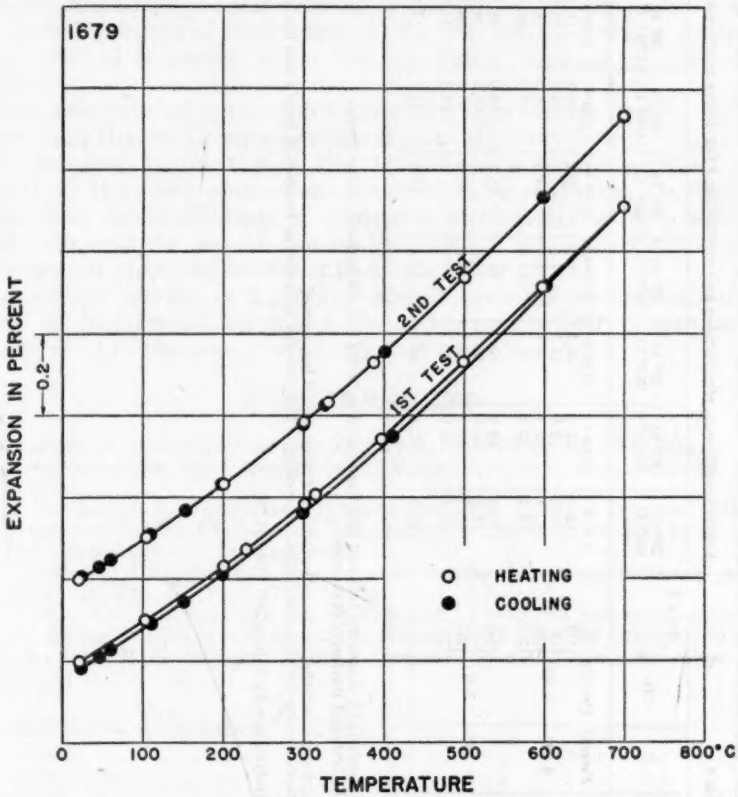

FIGURE 2.—*Linear thermal expansion of high-silicon cast iron containing molybdenun*

Si, 14.0; Mo, 3.0; Mn, 0.62; C, 0.91; S, 0.011; P, 0.088 percent.

Table 1 gives the coefficients of expansion and the coefficients of contraction that were obtained from the curves in figures 1 and 2. The maximum difference in all coefficients derived for any one temperature range was 0.4×10^{-6} for sample 1678 and 0.3×10^{-6} for sample 1679. The differences in the composition of the high-silicon cast iron containing 3 percent of molybdenum and of a similar cast iron containing 0.05 percent of molybdenum appear to have slight effect on the linear thermal expansion. The last column of table 1 indicates the permanent changes in length which occurred as a result of the heating and cooling in each test.

TABLE 1.—*Coefficients of linear expansion and contraction of annealed [a] high-silicon cast irons*

Sample [b]	Commercial name	Chemical composition [c]						Test [d]	Average coefficients of expansion and contraction [e] per degree centigrade						Change in length after heating and cooling [f]
		Si	Mn	C	S	P	Mo		20° to 100° C	20° to 200° C	20° to 300° C	20° to 400° C	20° to 500° C	20° to 600° C	20° to 700° C	
		Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*		×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	*Percent*
1678	Duriron	14.7	0.75	0.41	0.015	0.023	0.05	1H	12.2	12.9	13.7	14.6	15.4	16.1	16.5	−0.022
								1C	12.1	12.9	13.7	14.5		16.2	16.9	
								2H	12.4	13.1	13.9	14.7	15.5	16.3	16.8	−.002
								2C	12.2	12.9	13.7	14.6		16.3	16.8	
1679	Durichlor	14.0	.62	.91	.011	.088	3.0	1H	12.4	12.9	13.7	14.5	15.3	15.9	16.4	−.018
								1C	12.3	13.0	13.7	14.5		16.1	16.6	
								2H	12.2	12.9	13.7	14.6	15.3	16.1	16.7	+.003
								2C	12.2	13.0	13.7	14.4		16.1	16.6	
5074	Electrolytic iron								12.0	12.6	13.3	13.8	14.3	14.7	15.1	

[a] Heated to 1,700° F (927° C) and cooled slowly.
[b] Before the expansion tests, determinations of Knoop hardness numbers [5] of samples 1678 and 1679 were found to be 612 and 554 kg/mm², respectively.
[c] Determined by John F. Hewlett, Jr. and James I. Shultz, of the National Bureau of Standards.
[d] H represents heating and C cooling.
[e] For each coefficient of contraction on cooling (tests 1C and 2C), the temperature range indicated in the table should be reversed.
[f] Determined from the expansion curve on heating and the contraction curve (or final observation) on cooling. The plus sign indicates an increase in length and the minus sign a decrease in length.
[g] Added for comparison with high-silicon cast iron (data on electrolytic iron by Souder and Hidnert [6]).

The average coefficient of expansion of the high-silicon cast iron (without appreciable molybdenum) for the range from 20° to 100° C is in agreement with the higher of two values reported [1] in 1938. However, the average coefficient of expansion of the high-silicon cast iron (with 3 percent of molybdenum) for the temperature range from 20° to 100° C is nearly twice the low value reported in the same publication.

The coefficients of expansion of the two high-silicon cast irons are greater than the coefficients of expansion of electrolytic iron [2] reported by Souder and Hidnert [6]. For temperature ranges between 20° and 300° C, the coefficients of expansion of these cast irons are slightly greater than the coefficients of expansion of electrolytic iron, and for higher temperature ranges the coefficients of the former are appreciably greater than the coefficients of the latter.

The results shown in figures 1 and 2 revealed no indication of growth of the high-silicon cast irons on heating to 700° C, similar to that observed in the case of ordinary cast iron [6].

V. REFERENCES

[1] *Data sheets on materials of construction*, Chem. Met. Eng. **45**, 650 (1938).
[2] *Where high-silicon irons serve chemical industry*, Chem. Met. Eng. **36**, 541 (1921).
[3] E. S. Greiner, J. S. Marsch, and B. Stoughton, The Alloys of Iron and Silicon (Published for the Engineering Foundation by the McGraw-Hill Book Co., Inc., New York and London, 1933).
[4] W. Souder and P. Hidnert, *Measurements on the thermal expansion of fused silica*, Sci. Pap. BS **21**, 1 (1926) S524.
[5] F. Knoop, C. G. Peters, and W. B. Emerson, *A sensitive pyramidal-diamond tool for indentation measurements*, J. Research NBS **23**, 39 (1939) RP1220.
[6] W. Souder and P. Hidnert, *Thermal expansion of a few steels*, Sci. Pap. BS **17**, 611 (1922) S433.

WASHINGTON, December 27, 1943.

[2] See last line of table 1.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1582

Part of Journal of Research of the National Bureau of Standards, Volume 32, April 1944

ANALYTICAL DETERMINATION OF AROMATIC HYDROCARBONS BY ADSORPTION [1]

By Beveridge J. Mair and Alphonse F. Forziati [2]

ABSTRACT

A simple method is described for determining the amount of aromatic hydrocarbons in a mixture of hydrocarbons, as in the gasoline fraction of petroleum. The mixture to be analyzed is filtered through a column of solid adsorbent. An aromatic-free filtrate is obtained which contains the paraffin, naphthene, or olefin hydrocarbon which was associated in the original solution with the quantity of aromatic hydrocarbon which has been adsorbed. The concentration of an aromatic hydrocarbon in an unknown solution is determined by means of a calibration curve, established from experiments on known solutions which show the amount of aromatic-free filtrate produced by the standard adsorbent from solutions of various concentrations of the aromatic hydrocarbon. Results of experiments are given for several concentrations of eight binary solutions of an aromatic hydrocarbon with a paraffin or naphthene hydrocarbon and for three concentrations of a solution consisting of an aromatic hydrocarbon with a paraffin and an olefin. These experiments show that, if the temperature is controlled to within 1° C, the amount of aromatic hydrocarbon can be determined with an accuracy corresponding to 0.10 or less in the percentage by volume. A general procedure is given for determining the aromatic hydrocarbons in a "straight-run" gasoline and in a gasoline containing olefins.

CONTENTS

	Page
I. Introduction	152
II. General description	152
III. Apparatus and material	153
IV. Properties involved	153
V. Experimental procedure and data	156
VI. Discussion	159
1. Precision and sensitivity of the method	159
2. Effect of change in the operating temperature	159
3. Use of different lots of adsorbent	159
4. Variation in the composition of the paraffin and naphthene hydrocarbons in the solution	160
5. Variation in the composition of the aromatic hydrocarbons in the solution	161
6. Effect of the presence of olefin hydrocarbons	161
VII. Recommended procedure for analysis	161
1. Known aromatic hydrocarbon with paraffins and naphthenes	161
2. Known aromatic hydrocarbon with paraffins, naphthenes, and olefins	162
3. Aromatic hydrocarbons in the "straight-run" gasoline fraction of petroleum	163
4. Aromatic hydrocarbons in a gasoline containing olefins	164

[1] This investigation is a part of the work of Research Project 6 of the American Petroleum Institute, from whose research fund financial assistance has been received. The experimental work described herein was performed in the period from December 1941 to April 1942, and the manuscript was completed in May 1942.

[2] Research Associate at the National Bureau of Standards, representing the American Petroleum Institute.

I. INTRODUCTION

In this paper a simple and precise method is described for determining the amount of aromatic hydrocarbons in a mixture of hydrocarbons as in the gasoline fraction of petroleum. The method involves the process of adsorption, and the analysis is performed without actually separating the aromatic hydrocarbons.[3]

II. GENERAL DESCRIPTION

At a given temperature the amount of a given aromatic hydrocarbon selectively adsorbed by a "standard" quantity of a "standard" solid adsorbent, from a binary solution of the aromatic hydrocarbon with a given paraffin, naphthene, or olefin hydrocarbon, is a function of the concentration. When a solution containing aromatic, paraffinic, naphthenic, and olefinic hydrocarbons is filtered through a column of adsorbent, the resulting filtrate consists first of (a), material containing no aromatic hydrocarbons, next of (b), a small amount of material intermediate in composition between (a) and the original solution, and finally (c), the original solution. The intermediate part is apportioned (see section IV) between (a) and (c), so that there may be determined the amount of aromatic-free [4] material which would have been obtained had the break between (a) and (c) been infinitely sharp, with no intermediate portion. The concentration of the aromatic hydrocarbon in an unknown solution is determined by means of a calibration curve, established from experiments on known solutions which show the amount of aromatic-free filtrate produced by the standard adsorbent from solutions of various concentrations of the aromatic hydrocarbon.

When a solution of an aromatic hydrocarbon with a paraffin, naphthene, or an olefin hydrocarbon is filtered though a column of appropriate solid adsorbent, the first portion of solution comes in contact with successive layers of fresh adsorbent and its aromatic content is progressively reduced to zero. The first, or top, layer of adsorbent comes in contact with succeesive portions of solution having the initial concentration of aromatic hydrocarbon. This layer of adsorbent soon reaches a state of equilibrium between the aromatic hydrocarbon in the solution of the original concentration and the amount of the aromatic hydrocarbon adsorbed per unit quantity of adsorbent. As the solution progresses down the tube, successive layers of adsorbent come in contact and into equilibrium with solution of the initial concentration, which solution fills the macroscopic interstices of the adsorbent. With continued introduction of solution at the top of the column, the "equilibrium" zone, in which the adsorbed aromatic hydrocarbon is in equilibrium with solution of the initial concentration, extends farther and farther down the tube, forcing the nonaromatic material ahead of it, with a rather sharp region of demarcation between the two zones. Finally the "equilibrium" zone will reach the bottom, or last, layer of adsorbent, and at this point, solution of the original

[3] For a description of the methods used for separating substances by adsorption, see H. H. Strain, Chromatographic Adsorption Analysis, (Interscience Publishers, Inc., New York, N. Y., 1942), and L. Zechmeister and L. V. Cholnoky, Principles and Practices of Chromatography, John Wiley & Sons, Inc., New York, N. Y., 1942). With regard to the separation and recovery of aromatic hydrocarbons from petroleum by adsorption, see B. J. Mair and A. F. Forziati, J. Research NBS **32**, 165 (1944) RP1583.

[4] As used in this paper, the term "aromatic-free" refers to the material actually free from aromatic hydrocarbons plus that part of the intermediate portion allocated to it.

composition will just begin to emerge as filtrate from the bottom of the column of adsorbent.

III. APPARATUS AND MATERIAL

An apparatus which may be used for this method of analysis is shown in figure 1.[5] This apparatus is made of Pyrex glass and consists of the reservoir A; the main cylindrical section B, holding the bulk of the adsorbent; the filter tube section C, with the porous glass filter D for retaining the adsorbent; the stopcock E; and the graduated receiver F.[6]

The dimensions of the various parts for three convenient sizes of the apparatus are shown in table 1.

TABLE 1.—*Recommended dimensions and capacities for three sizes of the adsorption apparatus*

		Sizes		
		1	2	3
Adsorbent, mass of silica gel	g	75	37.5	18.75
Reservoir, volume	ml	500	300	200
Section B, inside diameter	mm	13.5	10.0	8.0
Section B, length	mm	750	750	650
Section C, inside diameter	mm	10.0	8.0	6.0
Section C, length	mm	80	80	60
Receiver, volume	ml	20	10	5
Receiver, length	mm	150	150	150
Receiver, graduations	ml	0.2	0.1	0.05

A refractometer is required for measuring the refractive index (usually n_D) of the filtrate, as well as an apparatus for determining the density of the aromatic-free filtrate. The necessary precision in the measurement of refractive index is about 0.0001 and that in the measurement of density about 0.001 g/ml.

Any suitably prepared solid adsorbent that selectivity adsorbs aromatic hydrocarbons may be used. In the experiments reported here, silica gel, 28 to 200 mesh in size, was used.[7] It is important to store the adsorbent in a bottle having a tightly fitting screw cap. In weighing the adsorbent, a tolerance of 0.05 percent is satisfactory.

IV. PROPERTIES INVOLVED

The experimental quantity to be determined is the volume or the mass (obtained by means of the density) of the aromatic-free filtrate. The volume of aromatic-free filtrate is determined from observations of the refractive index of the filtrate as a function of its volume. These

[5] In the experiments reported here, a simple adsorption tube without receiver was used, the gel was retained with a small plug of glass wool, and the filtrate fractions were collected in small bottles and measured in a graduated cylinder. For greater convenienc and possible increased precision; the apparatus shown in figure 1 is recommended.

[6] When operating on fractions containing substantial quantities of very volatile components, such as isopentane, it would be desirable to provide the receiver with a refrigerated jacket extending above the capillary outlet.

[7] Silica gel No. 659528-2000, Davison Chemical Corporation, Baltimore, Md.

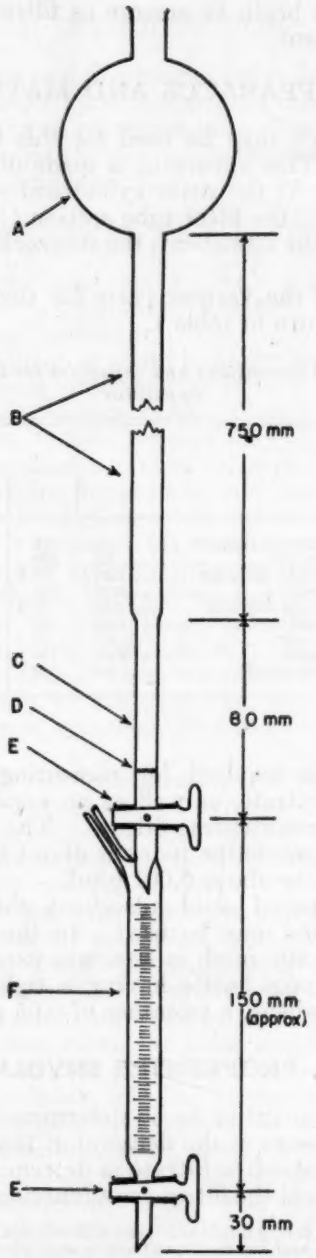

FIGURE 1.—*Apparatus for determining aromatic hydrocarbons by adsorption.*

A, Reservoir; *B*, main cylindrical section; *C*, filter section; *D*, glass filter with large pores; *E*, stopcock with straight bore, 2 mm in diameter; *F*, graduated receiver. The dimensions given are those for the size holding 75 g of adsorbent. See table 1 for the other sizes.

observations will be similar to those shown in figure 2(*A*), where there appear two plateaus of the refractive index (that of the material containing no aromatic hydrocarbons and that of the original solution) separated by a very small intermediate portion which may be considered as a mixture of these two. The intermediate portion is appropriately divided between the two plateaus (assuming additivity of the

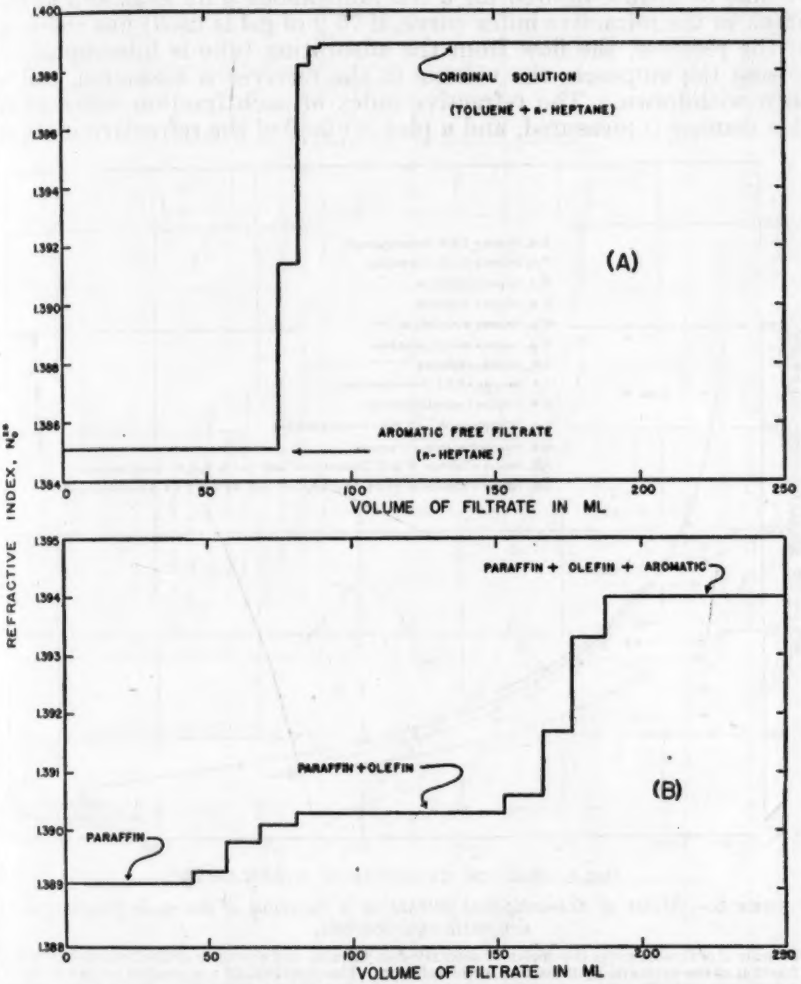

FIGURE 2.—*Refractive index of the filtrate as a function of its volume.*

The scale of ordinates gives the refractive index, $n^{25}D$ of the filtrate, and the scale of abscissas gives the volume of the filtrate in milliliters. The upper plot, 2(A), refers to a solution containing toluene and *n*-heptane. The lower plot, 2(B), refers to a solution containing toluene, "diisobutylene," and 2, 2,4-trimethylpentane.

refractive indices) in such a way as to show the volumes that would have been observed had the break between the two plateaus been infinitely sharp. Where it is desired to know the mass, the density of the portion containing no aromatic hydrocarbons is measured, and the mass computed from this and the measured volume, corrected by the appropriate amount of the intermediate portion.

V. EXPERIMENTAL PROCEDURE AND DATA

A known quantity of silica gel is placed in the adsorption tube (fig. 1), and packed with gentle tapping and it is retained on the porous glass filter. The solution, in whatever amount is required, is introduced into the reservoir at the top of the column. When the volume of filtrate desired for a fraction (about 5 ml near and at the break in the refractive index curve, if 75 g of gel is used) has collected in the receiver, the flow from the adsorption tube is interrupted by closing the stopcock, the volume in the receiver is measured, and is then withdrawn. The refractive index of each fraction collected in this manner is measured, and a plot is made of the refractive index as

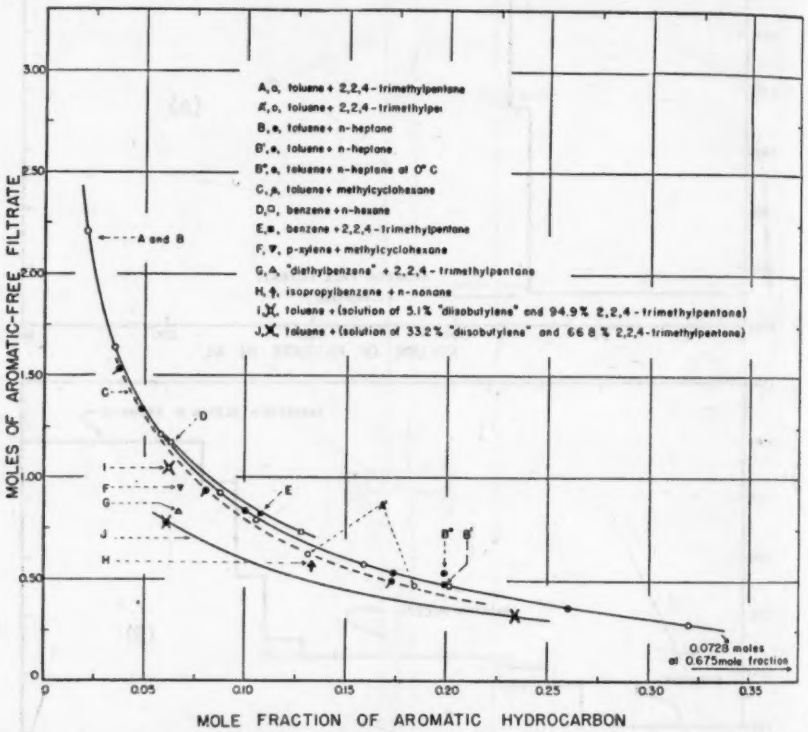

FIGURE 3.—*Moles of aromatic-free filtrate as a function of the mole fraction of the aromatic hydrocarbon.*

The scale of ordinates gives the moles of aromatic-free filtrate, and the scale of abscissas gives the mole fraction of the aromatic hydrocarbon in the solution. The observations represented by the B′ and A′ were made with silica gel samples I–b and II, respectively, whereas all the other observations involving silica gel were made with sample I–a. The observation represented by the point B° was made with sample I–b at 0° C. See text for explanation.

a function of the volume of filtrate.[8] (See fig. 2, A). Where the mass is to be known, the density of the portion actually free from aromatic hydrocarbons is measured. The intermediate portion is properly

[8] A somewhat different apparatus and modified procedure may be used to obtain a substantially continuous record of refractive index and volume. In this case, in addition to the main receiver, an auxiliary receiver with a known volume of about 0.3 ml is attached to the adsorption tube through a two-way stopcock. This auxiliary receiver is used to collect samples for refractive-index measurements. Readings of the total volume collected are made at the same time that samples are withdrawn for refractive-index measurements.

allocated (see section IV) to the two plateaus, and the total volume of aromatic-free filtrate recorded. This experiment is performed on the unknown solution and on enough solutions of known aromatic content to establish the calibration curve (see fig. 4), from which the aromatic content of the unknown may be determined.

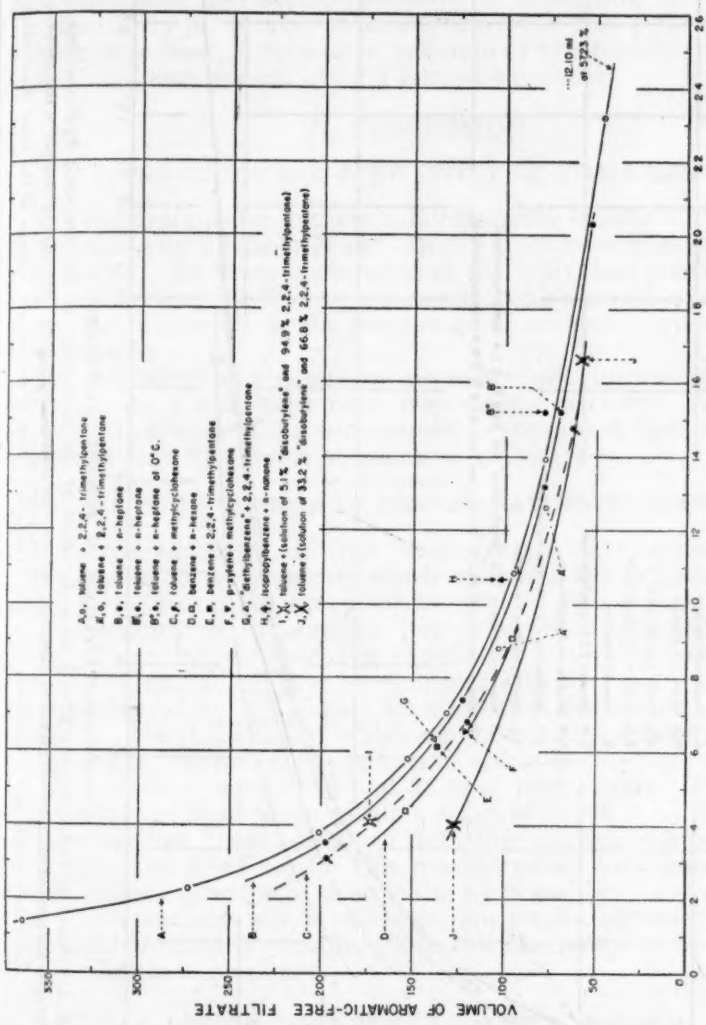
A-A, toluene + 2,2,4-trimethylpentane
A'-A', toluene + 2,2,4-trimethylpentane
B-B, toluene + n-heptane
B'-B', toluene + n-heptane
B°-B°, toluene + n-heptane at 0° C.
C-C, toluene + methylcyclohexane
D-D, benzene + n-hexane
E-E, benzene + 2,2,4-trimethylpentane
F-F, p-xylene + methylcyclohexane
G-G, "diethylbenzene" + 2,2,4-trimethylpentane
H-H, isopropylbenzene + n-nonane
I-I, toluene + isooctane of 51.1% "diisobutylene" and 94.9% 2,2,4-trimethylpentane)
J-J, toluene + isooctane of 33.2 % "diisobutylene" and 66.8 % 2,2,4-trimethylpentane)
12.10 ml or 5.23 %
VOLUME OF AROMATIC-FREE FILTRATE
PERCENTAGE BY VOLUME OF AROMATIC HYDROCARBON

FIGURE 4.—*Volume of aromatic-free filtrate as a function of the percentage of the aromatic hydrocarbon.* The scale of ordinates gives the volume of aromatic-free filtrate in milliliters, and the scale of abscissas gives the percentage by volume of the aromatic hydrocarbon in the solution. The observations represented by the points B' and A' were made with silica gel samples I-b and II respectively, whereas all the other observations involving silica gel were made with sample I-a. The observation represented by the point B° was made with sample I-b at 0° C. See text for explanation.

With a given apparatus and quantity of gel, the time required for the filtration depends on the volume to be filtered, which will be greater for the more dilute solutions. Practically all such filtrations can, however, be completed in from 1 to 4 hours.

To remove the used silica gel from the tube, it is first completely dried by passage of a stream of air and then poured out.

The results of a number of experiments, plotted in three different ways, are shown in figures 3, 4, and 5, for one or more concentrations of the following solutions:

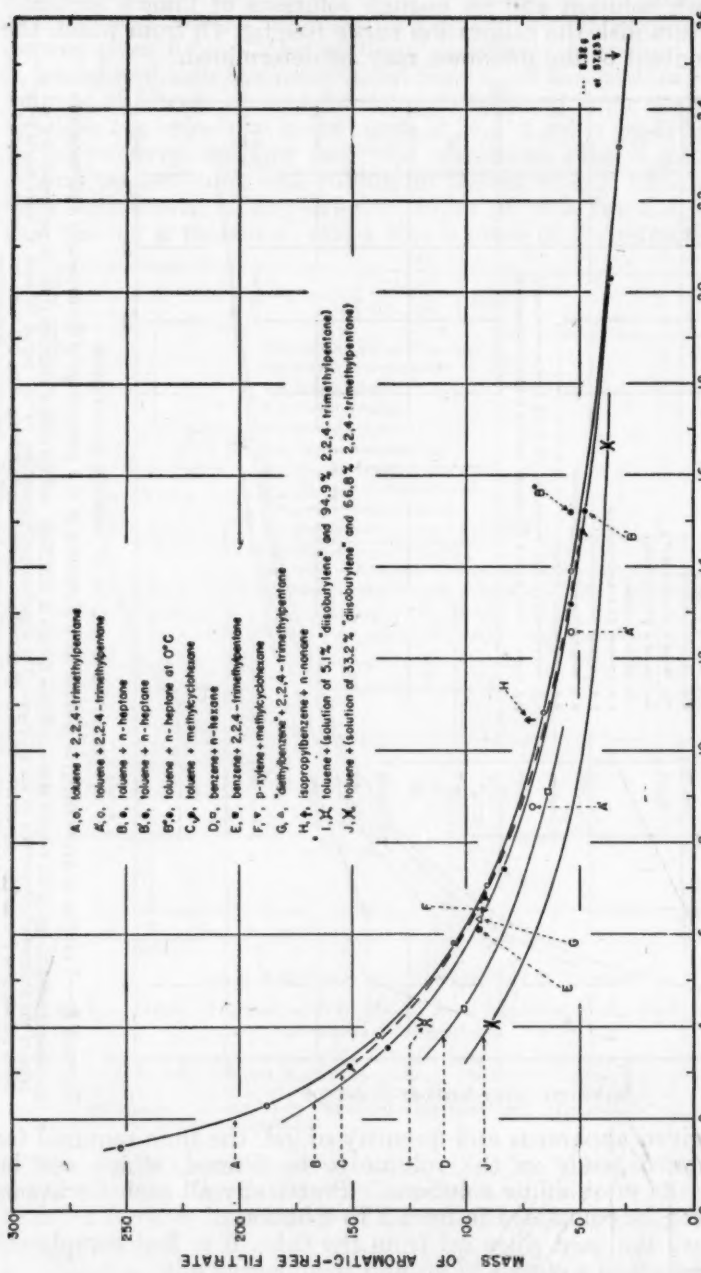

FIGURE 5.—*Mass of aromatic-free filtrate as a function of the percentage of the aromatic hydrocarbons.*

The scale of ordinates gives the mass of aromatic-free filtrate in milliliters, and the scale of abscissas gives the percentage by volume of the aromatic hydrocarbon in the solution.

The observations represented by the points B' and A' were made with silica gel samples I–b and II respectively, whereas all the other observations involving silica gel were made with sample I–a. The observation represented by the point B'' was made with sample I–b at 0 °C. See text for explanation.

A, toluene + 2,2,4-trimethylpentane; A′, toluene + 2,2,4-trimethylpentane; B, toluene + *n*-heptane; B′, toluene, + *n*-heptane; B°, toluene + *n*-heptane; C, toluene + methylcyclohexane; D, benzene + *n*-hexane; E, benzene + 2,2,4-trimethylpentane; F, *p*-xylene + methylcyclohexane; G, "diethylbenzene" + 2,2,4-trimethylpentane; H, isopropylbenzene + *n*-nonane; I, toluene + (solution of 5.1 percent of "diisobutylene" and 94.9 percent of 2,2,4-trimethylpentane); J, toluene + (solution of 33.2 percent of "diisobutylene" and 66.8 percent of 2,2,4-trimethylpentane).

VI. DISCUSSION

1. PRECISION AND SENSITIVITY OF THE METHOD

The observations for solution A fall along the smooth curve marked A, and those for solutions B and C along the curves marked B and C, respectively. In these cases, none of the individual points deviates from their respective lines by an amount which would correspond to more than about 0.1 in the percentage of aromatic hydrocarbon in the mixture.

The sensitivity of the method decreases with increasing aromatic content. At 5 and 20 percent, respectively, a change in the mass of aromatic filtrate of 1 g corresponds to changes of 0.06 and 0.66 in the percentage by volume of aromatic hydrocarbon.

2. EFFECT OF CHANGE IN THE OPERATING TEMPERATURE

With one exception, all the experiments were performed at the prevailing room temperature, which was recorded in each case and found to be within the range 23° to 28° C. To ascertain the effect of temperature on the analysis, one experiment was performed at 0° C. The result for the single experiment at 0° C is marked B° in figures 3, 4, and 5, and is to be compared with the result of an experiment performed at 28° C on the same solution, marked B′ in figures 3, 4, and 5. For this solution, which contained 15.23 percent by volume of toluene in *n*-heptane, the masses of aromatic-free filtrate obtained at 28° and 0° C were 47.73 and 53.48 g, respectively. If the temperature of the room stays within a range of about 5° C, the amount of aromatic-free filtrate obtained from this solution will be constant to within 0.46 g, which, for this concentration, corresponds to 0.25 in the volume percentage of aromatic hydrocarbon. For many purposes, this precision will be sufficient, but for the highest precision of which the method is capable, control of the temperature to within 1° C or better is necessary.

3. USE OF DIFFERENT LOTS OF ADSORBENT

Several samples of silica gel,[9] 28 to 200 mesh, were used. Samples I–a and I–b, although delivered to the laboratory at different times, were from the same manufactured lot. Sample II was from another manufactured lot. The observation represented by point B′ was made with sample I–b, whereas the observations for the rest of the B series were made with sample I–a. The point B′ falls on the curve

[9] No. 659528–2000. See footnote 7.

The observations represented by the points B′ and A′ were made with silica gel samples I–b and II respectively, whereas all the other observations involving silica gel were made with sample I–a. The observation represented by the point B° was made with sample I–b at 0° C. See text for explanation.

for the B series and shows that within the limits of these observations samples I–a and I–b have identical adsorptive capacities. The observations represented by the points A′ were made with sample II, whereas the rest of the observations for the A series were made with sample I–a. The points A′ fall below the curve for the rest of the A series and show that sample II has a lower adsorptive capacity than I–a or I–b. Since different manufactured lots appear to have somewhat different adsorptive capacities, it is necessary to calibrate each different lot of adsorbent with observations on one or two solutions of known concentration. It would appear desirable also to check each lot occasionally in the same manner.

4. VARIATION IN THE COMPOSITION OF THE PARAFFIN AND NAPHTHENE HYDROCARBONS IN THE SOLUTION

When, as in figure 3, the amount of aromatic-free filtrate is expressed in moles and the aromatic content in mole fraction, the curves A and B coincide. These curves represent, respectively, the solutions of toluene plus 2,2,4-trimethylpentane and of toluene plus *n*-heptane. Also the point E, for the solution benzene plus 2,2,4-trimethylpentane, falls on the curve D, which is for solutions of benzene plus *n*-hexane. That is, the amount of aromatic-free filtrate, when expressed in moles (for a given aromatic content expressed in mole fractions) is substantially independent of the particular paraffin which constitutes the nonaromatic portion of the solution. The curve C, in figure 3, for solutions of toluene plus methylcyclohexane, does not coincide with the curves A and B and shows the effect of changing the nonaromatic portion of the solution from a paraffin to a naphthene.

In figure 4, the amount of aromatic-free filtrate is expressed in terms of its volume and the aromatic content in terms of its percentage by volume. When these quantities are expressed in this manner, the curves A, B, and D show that the volume of aromatic-free filtrate (for a given percentage of a given aromatic hydrocarbon) decreases as the molecular weight of the paraffin hydrocarbon in the solution decreases. Curve D was obtained with solutions of benzene in *n*-hexane, and some of the decrease in the amount of the aromatic-free filtrate obtained for this series results from the fact that benzene rather than toluene was used as the aromatic component. However, by a comparison of point E with curve A, the effect of substituting benzene for toluene can be estimated, and it can be seen that a curve for solutions of toluene in *n*-hexane would be approximately as much below B as A is above B. Curve C, when compared with curve B, shows the effect of changing the nonaromatic portion of the solution from a paraffin to a naphthene hydrocarbon having the same number of carbon atoms per molecule. It is apparent that the volume of aromatic-free filtrate is less (for a given percentage of a given aromatic hydrocarbon) when the nonaromatic portion of the solution is a naphthene instead of a paraffin hydrocarbon having the same number of carbon atoms.

In figure 5 the amount of aromatic-free filtrate is expressed in terms of its mass and the aromatic content in terms of its percentage by volume. Curves A, B, and D show that the amount of aromatic-free filtrate decreases as the molecular weight of the paraffin hydrocarbon in the solution decreases. Curve C is in this case closer to curve B and slightly above it. This means that the mass of aromatic-free

filtrate, for a given percentage of a given aromatic hydrocarbon, is, within certain limits, approximately independent of the relative amounts of naphthenes and paraffines.

5. VARIATION IN THE COMPOSITION OF THE AROMATIC HYDROCARBONS IN THE SOLUTION

The single observations on the solutions E, F, G, and H involve aromatic hydrocarbons other than toluene. The point E, involving benzene, and the point F, involving "diethylbenzene," (a mixture of isomers) should be compared with the curve A, since 2, 2,4-trimethylpentane was the nonaromatic constituent in these cases, while the point G, involving *p*-xylene, should be compared with the curve C, since methylcyclohexane was the nonaromatic constituent in this case. When the results are expressed as in figure 3, it is evident that the number of moles of aromatic-free filtrate varies with the molecular weight of the aromatic hydrocarbon involved. When the results are expressed as in figures 4 and 5, the variations in the mass (or volume) of aromatic-free filtrate, due to changes in the aromatic portion of the solution, are comparatively small, and do not depend much on the molecular weight of the aromatic hydrocarbon involved.

6. EFFECT OF THE PRESENCE OF OLEFIN HYDROCARBONS

The behavior of a solution in which the nonaromatic portion contains an olefin, as well as a paraffin (or naphthene) hydrocarbon, is shown in figure 2 (B). In this case three plateaus are observed. The first plateau represents material free of both olefin and aromatic, the second plateau represents material free of the aromatic hydrocarbon, and the third plateau the original solution. The results of observations on three solutions containing an olefin are shown in figures 3, 4, and 5. In the experiment represented by point G, the nonaromatic portion contains, by volume, 5.14 percent of "diisobutylene" and 94.86 percent of 2, 2,4-trimethylpentane. The line through the points J represents solutions in which the nonaromatic portion contains, by volume, 33.2 percent of "diisobutylene" and 66.8 percent by volume of 2, 2,4-trimethylpentane. A comparison of the point I and curve J with curve A shows that there is a decrease in the amount of aromatic-free filtrate as the proportion of olefin in the nonaromatic portion is increased. In the region from 5 to 10 percent of aromatic content the amount of aromatic-free filtrate is reduced by an amount which corresponds to about 0.15 in the percentage of aromatics for each percent of olefin in the nonaromatic portion.

VII. RECOMMENDED PROCEDURE FOR ANALYSIS

1. KNOWN AROMATIC HYDROCARBON WITH PARAFFINS AND NAPHTHENES

Owing to the decrease in sensitivity of the method when applied to material of high aromatic content (section VI–1), it is advisable, if the aromatic content is greater than about 20 percent, to dilute the solution by a known amount (with pure paraffin or naphthene or paraffin-naphthene mixture) and to perform the analysis on the diluted mate-

rial, the concentration of which (in aromatic hydrocarbons) should preferably be in the range of 5 to 10 percent.

For solutions of low aromatic content the volume of material which must be filtered becomes very large. For this reason, if the quantity of material is limited, or if time is an important consideration, it is advisable to increase the aromatic content of solutions containing less than about 1.5 percent of aromatic hydrocarbons by adding a definite quantity of a known aromatic hydrocarbon. The analysis is then performed on the enriched solution.

After the aromatic content of the solution has been brought within the proper range, two filtration experiments are required to determine it accurately.

In the first of these, the larger apparatus with 75 g of silica gel is used. The volume (and density, if necessary) of the aromatic-free filtrate is determined, and an approximate value for the aromatic content is obtained, assuming a probable value for the molecular weight of the nonaromatic portion and using calibration curves similar to those given in figure 4 or 5, according to whether the volume or mass is being measured. A solution of this composition is then prepared, using the known aromatic hydrocarbon as one component and that portion of the filtrate actually free of aromatic hydrocarbon from the first experiment as the second component. In the second filtration experiment, which is performed with this solution, a smaller apparatus and the corresponding amount of silica gel is used. The volume or mass of aromatic-free filtrate is determined and converted to the quantity corresponding to 75 g of adsorbent. (The volume or mass of aromatic-free filtrate is directly proportional to the relative amounts of adsorbent used in the two experiments.) This quantity is now located on the calibration chart and a portion of a new calibration curve is drawn parallel to the others. With this curve and the volume or mass of aromatic-free filtrate obtained in the first experiment, there is determined accurately the percentage of aromatic hydrocarbons.

With this procedure, the naphthene-paraffin portion and the aromatic portion of the solution used for calibration are identical with those portions in the original solution. The accuracy of the determination is therefore the same as the precision, which, with suitable control of temperature, can be made very high, of the order of 0.10 percent or better.

2. KNOWN AROMATIC HYDROCARBON WITH PARAFFINS, NAPHTHENES, AND OLEFINS

The olefin content of the unknown mixture is first determined by an independent method. As pointed out in section VI–6, the olefin content need be known only to within ± 1 percent by volume to obtain the aromatic content to within ± 0.15 percent.

From this point on, the procedure is similar to that described in the preceding section, that is, two adsorption experiments are required. In the first of these, performed with 75 g of silica gel (or more if necessary) the volume or mass of aromatic-free filtrate is determined and an approximate value for the aromatic content obtained using calibration curves similar to those given in figures 4 and 5. The

solution to be used for calibration in the second experiment is prepared from that part of the filtrate from the first experiment which is free from both aromatic and olefin hydrocarbons, together with the amounts of the appropriate olefin and aromatic hydrocarbon required to give a solution of approximately the same composition as the original solution. From the results of the second experiment, a portion of a calibration curve is prepared, which, together with the results of the first experiment, can be used to ascertain accurately the aromatic content of the unknown.

Some uncertainty will be introduced in this analysis if substantial quantities of diolefins, particularly conjugated ones, are present, because these substances are more strongly adsorbed than monoolefins and, further, may be polymerized by the action of silica gel.

3. AROMATIC HYDROCARBONS IN THE "STRAIGHT-RUN" GASOLINE FRACTION OF PETROLEUM

The gasoline is first separated by distillation into three fractions, the first of which contains substantially all the benzene, the second all the toluene, and the third the higher-boiling aromatic hydrocarbons. Each fraction is then analyzed separately for its aromatic content. When analyses of this type are first instituted in a laboratory it is necessary to proceed in the manner described in section VII–1 that is, to use the aromatic-free portion from each fraction, together with the corresponding aromatic hydrocarbon to prepare solutions to be used for calibration. After the analysis of several gasolines, it may be possible to construct a mean calibration curve for each of the three fractions. Since the molecular weight of each fraction will be substantially the same for material from various sources, and since the variation due to change in the relative amount of paraffin and naphthene will be much less than that represented by the pure hydrocarbons methylcyclohexane and *n*-heptane shown in figure 5, it is evident that deviations from the mean calibration curves will be rather small.

If it is not required to know the amounts of the individual aromatic hydrocarbons, but only the total aromatic content, it is possible to operate on the entire gasoline fraction. In this case, the solution for calibration is prepared from the aromatic-free portion of the gasoline and a suitable aromatic hydrocarbon or mixture of aromatic hydrocarbons. Some uncertainty will be introduced into analyses performed in this manner so far as the aromatic hydrocarbon used in preparing the solution for calibration may not represent the aromatic composition of the unknown, but as already indicated (section VI, 5) the change in the position of the calibration curves (when volume or mass of aromatic-free filtrate is used) caused by substituting one aromatic hydrocarbon for another is not large. If the variation in the boiling-point range of the gasolines to be analyzed is not large (that is, if the mean molecular weights of the various gasolines are substantially the same), a mean calibration curve can be prepared for this fraction.

4. AROMATIC HYDROCARBONS IN A GASOLINE CONTAINING OLEFINS

The gasoline is first separated by distillation into three fractions. First, the olefin content of each fraction is determined by an independent method. When analyses of this type are first instituted in a laboratory it is necessary to proceed as described in section VII-2, that is, to use the aromatic-free, olefin-free portions from each fraction, together with the corresponding aromatic and olefin hydrocarbons, to prepare solutions to be used for calibration. After the analyses of a sufficient number of gasolines, it may be possible to construct for each of the three fractions a series of calibration curves representing different olefin contents, and thereby make it unnecessary to perform a calibrating experiment for each determination.

WASHINGTON, May 29, 1942.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1583

Part of Journal of Research of the National Bureau of Standards, Volume 32, April 1944

SEPARATION AND RECOVERY OF AROMATIC HYDROCARBONS FROM PARAFFINS AND NAPHTHENES BY ADSORPTION [1]

By Beveridge J. Mair and Alphonse F. Forziati [2]

ABSTRACT

A method is described for separating, by the process of adsorption, the aromatic hydrocarbons from their mixture with paraffin and naphthene (cycloparaffin) hydrocarbons, as in the gasoline or kerosine fractions of petroleum. The mixture is introduced into the top of a column containing an appropriate excess of solid adsorbent. A low-boiling paraffin hydrocarbon, such as pentane, butane, or propane, is then added in sufficient quantity to remove from the column the paraffin and naphthene hydrocarbons but not the aromatic hydrocarbons. The latter are then removed by adding an appropriate desorbing liquid, such as methanol. The paraffins, naphthenes, and pentane are thus obtained as a mixture from which the pentane is easily removed by distillation. The aromatic hydrocarbons are obtained as a mixture with pentane and methanol. The methanol is easily removed by extraction with water and the pentane by distillation.

This method of separation was tested on a known mixture of 17 pure hydrocarbons, the normal boiling points of which covered a range from 60° to 174° C and included all of the 5 normal paraffins from *n*-hexane through *n*-decane, the isoparaffin 2-methylpentane, the 4 normal alkyl cyclohexanes from cyclohexane through *n*-propylcyclohexane, and all of the 7 possible aromatic hydrocarbons from benzene through isopropylbenzene. The separation of the aromatic hydrocarbons from the paraffins and naphthenes was quantitative within the limits of measurement, and their recovery was complete within the normal operating loss of material in processing.

Experimental determinations were made of the quantity of aromatic hydrocarbon adsorbed per unit quantity of adsorbent, for a number of different binary solutions of aromatic hydrocarbons with paraffins or naphthenes, at several concentrations of the aromatic hydrocarbon, and with silica gel, carbon, magnesia, alumina, Filtrol, and Florisil as adsorbents. The results are displayed in the form of adsorption isotherms.

CONTENTS

	Page
I. Introduction	166
II. General description of the method	166
III. Statement of principles involved in the method	167
IV. Adsorptive capacity of various adsorbents	168
1. Solutions investigated and methods employed	168
2. Effect of temperature on the amount of aromatic hydrocarbon adsorbed	171
3. Variation in the composition of the paraffin and naphthene hydrocarbons in the solution	171
4. Variation in the composition of the aromatic hydrocarbons in the solutions	171
5. Comparison of various adsorbents	171

[1] This investigation is part of the work of Research Project 6 of the American Petroleum Institute, from whose research fund financial assistance has been received. The experimental work described herein was performed in the period from September 1941 to March 1942. The manuscript was first completed in June 1942 and revised in March 1943.

[2] Research Associate at the National Bureau of Standards, representing the American Petroleum Institute.

Page

V. Estimation of the amount of silica gel required for a given large-scale separation 172
VI. Apparatus and material 175
1. The adsorption tube 175
2. The adsorbent 176
3. The displacing liquid 176
4. The desorbing liquid 176
VII. Procedure 177
VIII. Experimental study 178
1. Determination of the amount of pentane required to remove methylcyclohexane from silica gel 178
2. Recovery of methylcyclohexane-heptane mixture from silica gel 179
3. Determination of the amount of methanol required to remove toluene and "diethylbenzene" from silica gel 179
4. Recovery of toluene from silica gel 181
5. Separation and recovery of a known mixture of aromatic hydrocarbons from a known mixture of naphthenes and paraffins 181
IX. Discussion of the separation of hydrocarbons by adsorption 182
X. References 183

I. INTRODUCTION

In this paper a method is described for separating, by the process of adsorption, the aromatic hydrocarbons from their mixture with paraffin and naphthene (cycloparaffin) hydrocarbons, as in the gasoline and kerosine fractions of petroleum. The method of adsorption used for this purpose is essentially that devised by the Russian botanist M. Tswett [1] [3] and commonly known as the Tswett method or the chromatographic method. Previous applications of this method to the separation of aromatic hydrocarbons involved principally hydrocarbons of high molecular weight and of biological importance.[4] While there are a number of reports on the use of the Tswett method in the field of petroleum chemistry [6, 7, 8, 9, 10, 11], the method does not appear to have been used for the separation and recovery of aromatic hydrocarbons from naphthene and paraffin hydrocarbons.

II. GENERAL DESCRIPTION OF THE METHOD

The petroleum fraction, a mixture of aromatic, naphthene, and paraffin hydrocarbons, is filtered through a column containing more than enough solid adsorbent to adsorb all of the aromatic hydrocarbons. The filtrate (if any) is (*a*) an aromatic-free mixture of paraffins and naphthenes. In addition to the aromatic hydrocarbons (*b*) which are retained within the column principally by adsorption, there are retained some paraffins and naphthenes (*c*) in the macroscopic interstices of the adsorbent and some which are weakly adsorbed.

The paraffins and naphthenes (*c*) are displaced by adding an appropriate low-boiling hydrocarbon in the liquid state (e. g. *n*-propane, *n*-butane, or *n*-pentane). The filtrate from this operation is (*d*) a mixture of the displaced paraffins and naphthenes together with the hydrocarbon used in displacing them. The filtrates (*a*) and (*d*) now contain the paraffins and naphthenes of the original charge. The original naphthenes and paraffins are separated by distillation from the low-boiling hydrocarbon in these fractions.

[3] Figures in brackets indicate the literature references at the end of this paper.
[4] See, for example, Chromatographic Adsorption Analysis [2] and the compilation recorded there from the work of Kuhn and Winterstein [3], Winterstein and Schön [4], and Winterstein, Schön, and Vetter [5].

The aromatic hydrocarbons on the adsorbent, together with the low-boiling hydrocarbon in the column, are displaced by the addition of a substance which is more strongly adsorbed than the aromatic hydrocarbons. The added substance may be methanol, in which case the aromatic hydrocarbons are obtained as a mixture with the low-boiling hydrocarbon and methanol. The methanol may be removed by extraction with water and the low-boiling paraffin removed by distillation, or, if pentane is used, both the methanol and the pentane may be removed by distillation, provided the amount of the pentane is more than sufficient to remove the methanol as an azeotropic mixture.

The adsorbent may then be reactivated for the next cycle.

III. STATEMENT OF PRINCIPLES INVOLVED IN THE METHOD

Certain of the principles involved in the process of adsorption are now reasonably well understood [12, 13, 14]. When a solution of an aromatic hydrocarbon with a paraffin or a naphthene is filtered through a column of solid adsorbent, the first portion of solution comes into contact with successive layers of fresh adsorbent and its aromatic content is progressively reduced to zero. The first, or top, layer of adsorbent comes into contact with successive portions of solution having the initial concentration of aromatic hydrocarbons. This layer of adsorbent soon reaches a state of equilibrium between the aromatic hydrocarbons in the solution of the original concentration and the amount of aromatic hydrocarbon adsorbed per unit quantity of adsorbent. As the solution moves down the tube, successive layers of adsorbent come into contact and into equilibrium with solution of the initial concentration. Thus, extending downward from the top layer of adsorbent, a zone is formed in which the adsorbed aromatic hydrocarbon is in equilibrium with solution of the initial concentration, which solution fills the macroscopic interstices of the adsorbent. With continued introduction of solution at the top of the column, this equilibrium zone extends farther and farther down the tube, forcing the aromatic-free material ahead of it, with (if the filtration is not too rapid) a comparatively narrow region between the equilibrium zone and the aromatic-free portion. Finally, the equilibrium zone will reach the bottom or last layer of adsorbent, and, at this point, solution containing the initial concentration of aromatic hydrocarbon will just begin to emerge as filtrate from the bottom of the column of adsorbent.

It is apparent that the treatment of a solution of an aromatic hydrocarbon in a paraffin or naphthene in the manner just described may yield a portion of the charge as aromatic-free material, but that a quantitative separation of paraffin or naphthene hydrocarbons from aromatic hydrocarbons is not possible by this process alone. The complete separation of a paraffin or naphthene hydrocarbon from an aromatic is possible if the ratio of the quantity of charge to adsorbent is selected (as described in section V) so that, when the entire charge has been introduced into the column of adsorbent, the equilibrium zone extends only part way down the adsorbent column. There is then introduced into the top of the column the displacing hydrocarbon (e. g., *n*-pentane). When the first portion of this solvent enters the first, or top, layer of adsorbent, it dissolves some of the aromatic

hydrocarbons. As successive portions pass through the top layer its aromatic content is progressively reduced to zero. In the meantime the original solution is displaced down the column and comes into contact with fresh adsorbent, and consequently the lower edge of the equilibrium zone moves downward. The net effect of this process is a downward movement of the equilibrium zone, together with a substitution of the displacing hydrocarbon for the paraffin or naphthene originally in the equilibrium zone. If sufficient adsorbent and displacing liquid have been used, the original paraffin or naphthene will be completely displaced from the column before the equilibrium zone reaches the bottom and before aromatic material appears in the filtrate.

IV. ADSORPTIVE CAPACITY OF VARIOUS ADSORBENTS

1. SOLUTIONS INVESTIGATED AND METHODS EMPLOYED

To find the best adsorbent to use in this method of separation, experimental determinations were made of the quantity of aromatic hydrocarbon adsorbed per unit quantity of adsorbent, for a number of different binary solutions of aromatic hydrocarbons with paraffins and naphthenes, at several concentrations of the aromatic hydrocarbon, and with silica gel, carbon, magnesia, alumina, Filtrol, and Florisil as adsorbents.

With silica gel [5] as the adsorbent, data were obtaind for one or more concentrations of the following solutions: A, toluene+2,2,4-trimethylpentane; A′, toluene+2,2,4-trimethylpentane; A^2, toluene+2,2,4-trimethylpentane; A^3, toluene+2,2,4-trimethylpentane; B, toluene+*n*-heptane; B′, toluene+*n*-heptane; B°, toluene+*n*-heptane; C, toluene+*n*-hexane; D, toluene+methylcyclohexane; E, benzene+*n*-hexane; F, benzene+2,2,4-trimethylpentane; G, *p*-xylene+methylcyclohexane; H, "diethylbenzene"+2,2,4-trimethylpentane; I, isopropylbenzene+*n*-nonane.

All the observations for the solutions listed, except for solution B°, were made at the prevailing room temperature, which was recorded in each case and found to be within the range 23° to 28° C. Except in those cases where the letter representing the solution is characterized with a superscript, one lot of the regular silica gel, sample I–a, (see section IV–5) was used. The data, which are displayed in the form of adsorption isotherms in figures 1 and 2, were obtained from filtration experiments on solutions of known concentration, using 75 g of silica gel, and with a ratio of length to diameter of the column of adsorbent about 40 to 1. The volume of aromatic-free filtrate, corrected for the small intermediate portion, was determined as described previously [11]. The quantity of aromatic adsorbed was computed on the assumption that no paraffin or naphthene was adsorbed.[6] On this basis the quantity of aromatic adsorbed

[5] In this paper the term "silica gel," in any given particle size, when used without qualification, refers to material stabilized at the "normal" temperature and designated as No. 659528–2000 (28 to 200 mesh) or No. 659528–420 (28 to 42 mesh), Davison Chemical Corp., Baltimore, Md. In several instances, silica gel stabilized at higher than the "normal" temperature and designated as No. 859528–2000 (28 to 200 mesh) was used and is so indicated.

[6] Actually a small amount of paraffin or napthene is adsorbed and consequently the correct values for the amount of aromatic adsorbed will be slightly greater than the values shown in figures 1 and 2.

is that quantity which in the original solution was associated with the portion rendered aromatic-free. The equilibrium concentration is in this case the concentration of the original solution.

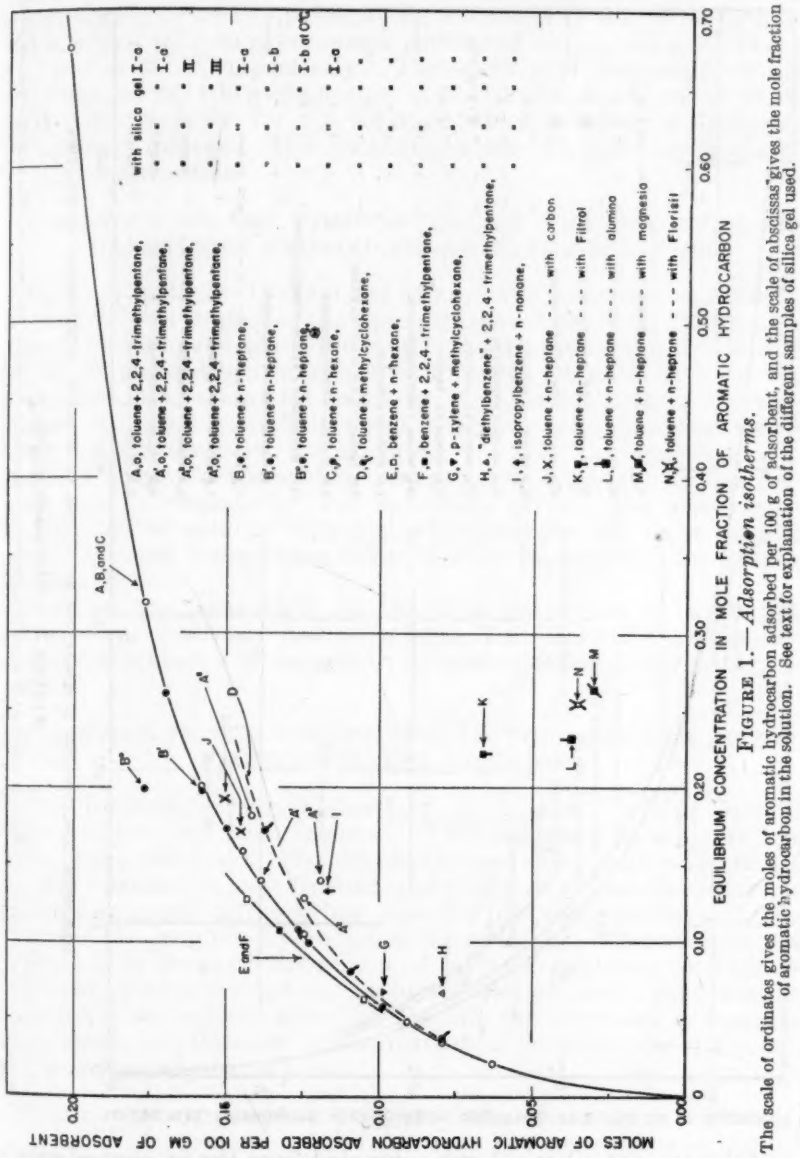
MOLES OF AROMATIC HYDROCARBON ADSORBED PER 100 GM OF ADSORBENT
0.20
0.15
0.10
0.05
0.00
0
0.10
0.20
0.30
0.40
0.50
0.60
0.70
EQUILIBRIUM CONCENTRATION IN MOLE FRACTION OF AROMATIC HYDROCARBON
A,o, toluene + 2,2,4-trimethylpentane, with silica gel I-a
A',o, toluene + 2,2,4-trimethylpentane, " " I-a'
A'',o, toluene + 2,2,4-trimethylpentane, " " II
A''',o, toluene + 2,2,4-trimethylpentane, " " III
B,•, toluene + n-heptane, " " I-a
B',•, toluene + n-heptane, " " I-b
B'',•, toluene + n-heptane, " " I-b at 0°C
C,▲, toluene + n-hexane, " " I-a
D,▼, toluene + methylcyclohexane, " "
E,□, benzene + n-hexane, " "
F,■, benzene + 2,2,4-trimethylpentane, " "
G,▼, p-xylene + methylcyclohexane, " "
H,◆, "diethylbenzene" + 2,2,4-trimethylpentane, " "
I,◆, isopropylbenzene + n-nonane, " "
J,X, toluene + n-heptane --- with carbon
K,●, toluene + n-heptane --- with Filtrol
L,●, toluene + n-heptane --- with alumina
M,✕, toluene + n-heptane --- with magnesia
N,X, toluene + n-heptane --- with Florisil
A,B,and C
E and F
G
H
K
L
N
M

FIGURE 1.—*Adsorption isotherms.*

The scale of ordinates gives the moles of aromatic hydrocarbon adsorbed per 100 g of adsorbent, and the scale of abscissas gives the mole fraction of aromatic hydrocarbon in the solution. See text for explanation of the different samples of silica gel used.

The results of observations with carbon, alumina, magnesia, Filtrol, and Florisil, as the adsorbents, and represented, respectively, by the letters J, L, M, K, and N for solutions of toluene and *n*-heptane,

are also shown in figures 1 and 2. These results were obtained from experiments performed at 25° C, in which a known weight of adsorbent was shaken with the solution until equilibrium was attained

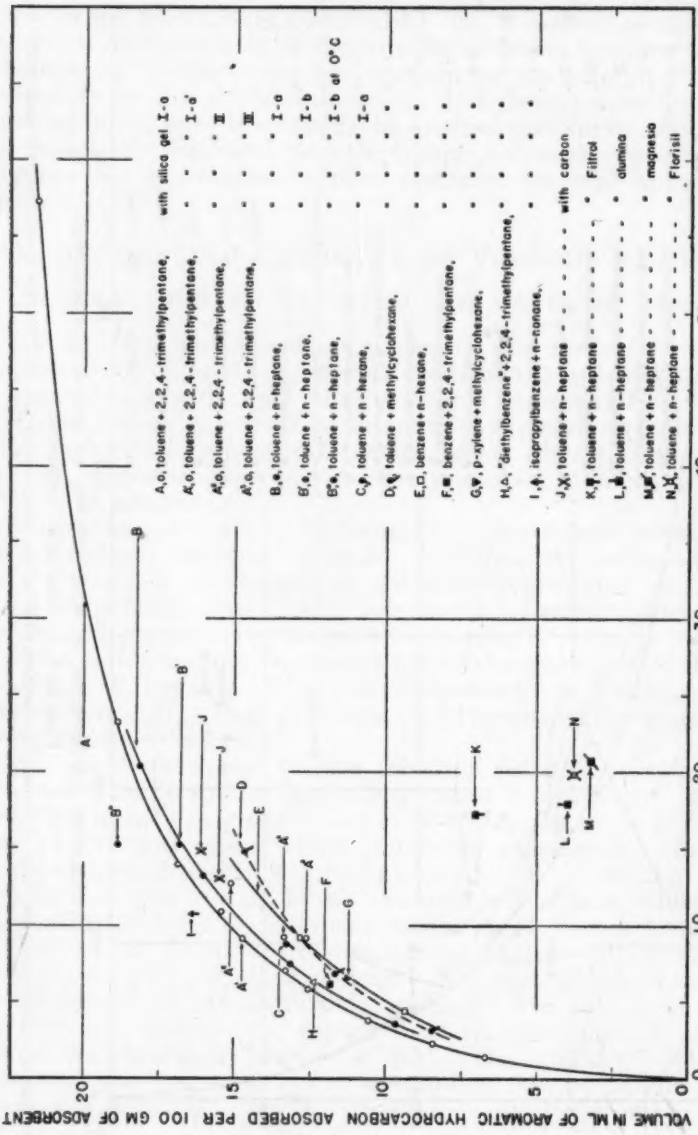
A,o, toluene + 2,2,4-trimethylpentane, with silica gel I-a
A',o, toluene + 2,2,4-trimethylpentane, " " I-a'
A'',o, toluene + 2,2,4-trimethylpentane, " " II
A''',o, toluene + 2,2,4-trimethylpentane, " " III
B,•, toluene + n-heptane, " " I-a
B',•, toluene + n-heptane, " " I-b
B'',•, toluene + n-heptane, " " I-b at 0°C
C,▲, toluene + n-hexane, " " I-a
D,▼, toluene + methylcyclohexane, " " "
E,□, benzene + n-hexane, " " "
F,■, benzene + 2,2,4-trimethylpentane, " " "
G,▼, p-xylene + methylcyclohexane, " " "
H,◇, "diethylbenzene"+2,2,4-trimethylpentane, " " "
I,◆, isopropylbenzene + n-nonane, " " "
J,X, toluene + n-heptane - - - - - - - - with carbon
K,▼, toluene + n-heptane - - - - - - - - Filtrol
L,■, toluene + n-heptane - - - - - - - - alumina
M,X, toluene + n-heptane - - - - - - - - magnesia
N,X, toluene + n-heptane - - - - - - - - Fuller's earth
VOLUME IN ML OF AROMATIC HYDROCARBON ADSORBED PER 100 GM OF ADSORBENT
EQUILIBRIUM CONCENTRATION IN PERCENTAGE BY VOLUME OF AROMATIC HYDROCARBON IN SOLUTION
0
5
10
15
20
0
10
20
30
40
50
60
70

FIGURE 2.—*Adsorption isotherms.*

The scale of ordinates gives the volume in milliliters of aromatic hydrocarbon adsorbed per 100 g of adsorbent, and the scale of abscissas gives the percentage by volume of aromatic hydrocarbon in the solution. See text for explanation of the different samples of silica gel used.

and the amount adsorbed was computed from the amount of solution and its change in concentration.[7]

[7] Experiments performed in this manner with silica gel as the adsorbent gave results which, though somewhat less precise, were in substantial agreement with those from the filtration experiments. To avoid unduly complicating figures 1 and 2 these results are not included.

2. EFFECT OF TEMPERATURE ON THE AMOUNT OF AROMATIC HYDROCARBON ADSORBED

The effect of temperature on the amount of aromatic hydrocarbon adsorbed may be noted by comparing the points B° and B′ in figures 1 and 2, which refer to experiments performed on the same solution at 0° C and at 28° C, respectively. The amounts of aromatic hydrocarbon adsorbed per 100 g of silica gel at 0° C and at 28° C are 16.26 and 14.51 g, respectively, for this solution, which contains 15.23 percent by volume of toluene. This is a change of about 0.4 percent per degree for this concentration.

3. VARIATION IN THE COMPOSITION OF THE PARAFFIN AND NAPHTHENE HYDROCARBONS IN THE SOLUTION

When, as in figure 1, the moles of aromatic hydrocarbon adsorbed are plotted with respect to the concentration of aromatic hydrocarbon in mole fraction, a single curve may be used to represent the data for any of the paraffin hydrocarbons with a given aromatic hydrocarbon. Thus, the observations for solutions A, B, and C, which represent toluene with 2,2,4-trimethylpentane, *n*-heptane, and *n*-hexane, respectively, fall substantially on a single curve. Also, the observations for solutions E and F, representing benzene with 2,2,4-trimethylpentane and *n*-hexane, respectively, fall on a single curve. The observations for solutions of toluene with methylcyclohexane fall on a separate curve, D, which is somewhat below that for toluene with the paraffin hydrocarbons.

Since, in the separation process, it is convenient to work with volumes, the results are plotted in figure 2 in terms of the volume of aromatic adsorbed with respect to its concentration in percentage by volume.

4. VARIATION IN THE COMPOSITION OF THE AROMATIC HYDROCARBONS IN THE SOLUTIONS

The observations on solutions E, F, G, H, and I involve aromatic hydrocarbons other than toluene. When expressed as in figure 1, in terms of the moles of aromatic hydrocarbons adsorbed with respect to the concentration in mole fraction, the results show that the number of moles of aromatic hydrocarbon adsorbed decreases as the molecular weight of the aromatic hydrocarbon is increased. When expressed as in figure 2, in terms of the volume of aromatic adsorbed with respect to the concentration in percentage by volume, the results show that the variation in the volume adsorbed, for different aromatics, is comparatively small, and depends to some extent on the structure of the individual aromatic hydrocarbons.

5. COMPARISON OF VARIOUS ADSORBENTS

Several lots of silica gel [8] were used for these observations. Lots I–a and I–a′ were stabilized at the normal temperature and were of 28- to 200- and 28- to 42-mesh size, respectively. Lot I–b, although delivered to the laboratory at a later date than was I–a, was from the

[8] See footnote 5.

same manufactured batch. Lot II was prepared in the same way as lots I–a and I–b but was from another manufactured batch. Lot III was of 28- to 200-mesh size but was stabilized at higher than the normal temperature.

The observation on solution B′ was made with lot I–b, and is in accord with the rest of the observations for the B series, which were made with lot I–a. The observation for solution A′, which was made with lot I–a′, is in accord with the rest of the observations for the A series, which were made with lot I–a, and shows that these two lots of different particle size have substantially the same adsorptive capacity. The observations represented by the points A^2 were made with lot II, and the points fall substantially below the curve for the rest of the A series, which indicates a lower adsorptive capacity. The observation on solution A^3 was made with lot III. The point A^3 falls well below the curve for the A series, and indicates that the adsorptive capacity of the silica gel stabilized at the higher temperature is less than that of the material stabilized at the normal temperature. It may be noted, however, that because the apparent density of the silica gel stabilized at the normal temperature is less than that of the other, the adsorptive capacities, per unit volume, do not differ greatly.

The points J, L, M, K, and N represent the results of observations with solutions of toluene in *n*-heptane when carbon, alumina, magnesia, Filtrol, and Florisil, respectively, were used as adsorbents.[9]

By a comparison of the points J, K, L, M, and N with curve B, it is evident that of these adsorbents, and for the systems under investigation, only carbon has an adsorptive capacity which approaches that of silica gel. However, the apparent density of activated carbon is less than that of silica gel, and, on a volume basis, its adsorptive capacity is substantially less than that of silica gel.

V. ESTIMATION OF THE AMOUNT OF SILICA GEL REQUIRED FOR A GIVEN LARGE-SCALE SEPARATION

Before an estimate can be made of the quantity of silica gel required to separate a given solution, it is necessary to know the concentration of aromatic hydrocarbon and the amount of aromatic hydrocarbon absorbed per unit mass of adsorbent from a solution of the given concentration. The aromatic content of the solution may be determined from a preliminary small-scale experiment, in which a portion is filtered through a standard quantity of silica gel [11]. From the volume of aromatic-free filtrate produced in this experiment and the concentration of aromatic hydrocarbon in the original solution, the amount of aromatic hydrocarbon adsorbed per gram of adsorbent can also be determined.

It is also necessary to determine experimentally the amount of displacing liquid required to wash the adsorbent completely free from the original paraffin-naphthene mixture and carry it into the filtrate (see section VIII–1).

[9] The identifying characteristics of these adsorbents are: Columbia Activated Carbon, Grade F, size 20 to 48 mesh, Carbide & Carbon Chemicals Corp., New York, N. Y.; Activated Alumina, Grade A, size 80 to 300 mesh, Aluminum Ore Co., East St. Louis, Ill.; Adsorptive Powdered Magnesia No. 2641, impalpable powder, California Chemical Co., Newark, Calif.; Filtrol (prepared commercial fuller's earth) X-215, M–162, size 60 to 100 mesh, special lot supplied by G. Calingaert, of the Ethyl Gasoline Corp., for this experiment; Florisil (prepared commercial fuller's earth), analytical adsorbent, 60 to 100 mesh, Floridin Co., Warren, Pa.

The estimation of the amount of silica gel required for the separation of a simple binary mixture of an aromatic and a paraffin hydrocarbon, using as a displacing liquid another paraffin hydrocarbon, is made in the following manner: As stated in section III, the displacing liquid, in addition to substituting itself for the paraffin originally present, causes a downward movement of the equilibrium zone. In the ideal case involving no mixing of the displacing liquid and the paraffin hydrocarbon of the original solution, the column would be divided into three zones: a zone at the top containing only the displacing liquid; a second zone in which the adsorbed aromatics are in equilibrium with those in the displacing liquid; and a third zone containing only the original paraffin. The minimum quantity of adsorbent required would be that quantity which would just allow the original paraffin to pass completely from the column but would not allow any of the liquid from the second zone to pass out of the column. If the displacing liquid simply forces the solution ahead of it, without any mixing between it and the original solution, and if the break between the equilibrium zone and the aromatic-free portion ahead of it is infinitely sharp, the theoretical minimum quantity of adsorbent is given by the equation

$$y=\frac{n_a}{Q_a}=\frac{n_s x_a}{Q_a}. \tag{1}$$

Here n_a is the number of moles of aromatic hydrocarbon in the solution, Q_a is the adsorptive capacity of the adsorbent in moles of aromatic hydrocarbon per gram of adsorbent for the given concentration of aromatic hydrocarbon, y is the number of grams of adsorbent, n_s is the number of moles of original solution, and x_a is the mole fraction of aromatic hydrocarbon.

The ideal case just described does not represent the actual situation accurately, because in practice there is some mixing between the displacing liquid and the original solution. Furthermore, the amount of the original paraffin or naphthene that is actually adsorbed must be desorbed.[10] For these reasons it is necessary to pass an additional amount of the displacing liquid through the column to wash out the original paraffin completely and to carry it into the filtrate.

To estimate the total quantity of adsorbent required, the process may be regarded as taking place in a series of steps. In the first step, the quantity of adsorbent required to adsorb the aromatic hydrocarbons from the original solution may be computed. Similarly, in each succeeding step there may be computed the quantity of adsorbent which is necessary to adsorb the aromatic hydrocarbons from the displacing liquid required in the preceding step. The quantity of adsorbent required in the first step is that given by the following equation, which is equation 1 converted to a volume basis:

$$y=\frac{V_s c_a}{Q_{va}} \tag{2}$$

Here V_s is the volume of the solution, c_a is the volume fraction of aromatic hydrocarbon in the solution, and Q_{va} is the adsorptive capacity in volume of aromatic hydrocarbon per gram of adsorbent.

[10] See footnote 6.

If b is the volume of displacing liquid required per gram of adsorbent to remove the original paraffin completely from the first step, then

$$\frac{V_s c_a}{Q_{va}} b$$

is the volume of displacing liquid required in the first step. If c_a' is the concentration in volume fraction of aromatic hydrocarbon in the displacing solution,

$$\frac{V_s c_a}{Q_{va}}\left(\frac{b c_a'}{1-c_a'}\right)$$

is the volume of aromatic hydrocarbon to be adsorbed. If Q_{va}' is the adsorptive capacity of the adsorbent for a solution of the concentration c_a', the quantity of adsorbent required in the second step is

$$\frac{V_s c_a}{Q_{va}}\left[\frac{c_a'}{Q_{va}'}\left(\frac{b}{1-c_a'}\right)\right].$$

The total quantity of adsorbent required for all steps is

$$y=\frac{V_s c_a}{Q_{va}}\left[1+\frac{c_a'}{Q_{va}'}\left(\frac{b}{1-c_a'}\right)+\frac{c_a' c_a''}{Q_{va}' Q_{va}''}\left(\frac{b}{1-c_a'}\right)\left(\frac{b}{1-c_a''}\right)+\cdots\right] \quad (3)$$

Assuming that $c_a'=c_a''=c_a'''=\ldots$ and that $Q_{va}'=Q_{va}''=Q_{va}'''=\ldots$, and substituting k for c_a'/Q_{va}', there is obtained

$$y=\frac{V_s c_a}{Q_{va}}\left[1+k\left(\frac{b}{1-c_a'}\right)+k^2\left(\frac{b}{1-c_a'}\right)^2+\cdots\right]=\frac{V_s c_a}{Q_{va}}\left[\frac{1}{1-\frac{kb}{1-c_a'}}\right]$$

$$=\frac{V_s c_a}{Q_{va}}\left[\frac{1-c_a'}{1-c_a'-kb}\right]. \quad (4)$$

In determining values to be used for k and b, it is desirable to consider separately the case of solutions with greater than 20-percent aromatic content from the case of those with less, for the reasons indicated below.

With pentane as the displacing liquid and with the natural rate of flow obtained, using well-packed silica gel of 28 to 200 mesh, the aromatic content of the displacing liquid is usually less than about 15 volume percent for all concentrations of the original solution above about 20 volume percent. To be safe, however, c_a' may be taken as 0.20 and the corresponding value 0.18 taken for Q_{va}', so that $k=c_a'/Q_{va}'$ becomes about 1.1. In addition to the simple volume displacement of the original solution, the displacing liquid must also desorb and substitute itself for any of the original paraffins and naphthenes which have been adsorbed. The quantity of displacing liquid required for this purpose depends on the equilibrium between the displacing liquid and the original paraffin and naphthene, and on how closely this equilibrium is approached in the desorption process. This in turn depends on the rate of filtration. With pentane as the displacing liquid, and with the natural rate of flow obtained with well-packed silica gel of 28 to 200 mesh, an allowance of 0.35 to 0.40 ml of pentane per gram of silica gel usually suffices to remove the original paraffins and naphthenes and to carry them into the filtrate (see section VIII–1). That is to say, b may be taken as equal to 0.35 ml/g. Substituting the values for k, b, and c_a' in equation

5 for all solutions with an aromatic content greater than about 20 volume percent, the quantity of silica gel required becomes

$$y=2\frac{V_s c_a}{Q_{va}}. \tag{5}$$

For original solutions containing less than about 20 volume percent of aromatic hydrocarbon, the difference between the concentration of aromatics in the original solution and in the displacing liquid (*n*-pentane) is much less than for solutions containing more than about 20 percent by volume of aromatic hydrocarbon, and in the absence of any better method for estimating the concentration of aromatic hydrocarbon in the displacing liquid, c'_a may be taken as equal to c_a, and Q'_{va} may be taken as equal to Q_{va}. Thus for solutions containing less than about 20 volume percent of aromatic hydrocarbons, the required quantity of silica gel is

$$y=\frac{V_s c_a}{Q_{va}}\left[\frac{1-c_a}{1-c_a-kb}\right]. \tag{6}$$

It should be emphasized that equations 5 and 6 will give approximately the quantity of silica gel required only for silica gel of 28 to 200 mesh, in well-packed columns of comparatively narrow diameter (2.5 to 5 cm). With columns of wide diameter the rates of flow at various distances from the periphery are likely to differ appreciably. Thus the boundaries of the zones will not be substantially normal to the walls of the column but may be concave, convex, or irregular in shape. A greater quantity of adsorbent will therefore be required. For silica gel of larger particle size, with which the rate of flow (when not controlled) is rapid, a greater volume of displacing liquid will be required, and the concentration of aromatic hydrocarbons in the displacing liquid may be considerably below the values given in this section.

VI. APPARATUS AND MATERIAL

1. THE ADSORPTION TUBE

The only apparatus specifically required for the adsorption method is a cylindrical tube of a volume sufficient to hold the quantity of adsorbent required for the given separation. The ratios of length to diameter of the tubes prepared in this laboratory are generally not less than 30 to 1. The adsorption column may be made out of any material that will not react with the hydrocarbons or the displacing or desorbing liquids. Some arrangement for retaining the adsorbent within the column must also be provided. In the case of the Pyrex glass columns used in this laboratory, the adsorbent is retained with a small plug of glass wool fitted into the bottom of the adsorption column, which is drawn down and sealed to a tube of smaller dimensions. It is desirable to include a stopcock in the small tube at the bottom of the column, so that the flow of filtrate may be interrupted when it is desired to change the receiver. In the filtration process, there is a rise in temperature due to the heat of adsorption, and it is desirable to prevent loss by evaporation by refrigerating the receiver. Precautions should also be taken to prevent loss by evapo-

ration at the top of the column, as by venting through a capillary tube if the operation is performed at atmospheric pressure.

If it is desired to reactivate the adsorbent in the column used for the adsorption, the column should preferably be constructed of some metal such as stainless steel. In this case, additional equipment for maintaining the column at the desired temperature, for introducing steam and air or an inert gas and for condensing the excess desorbing liquid must be provided.

2. THE ADSORBENT

Any solid adsorbent which selectively adsorbs aromatic hydrocarbons may be used. Practically, however, it is desirable that the adsorbent have as large an adsorptive capacity per unit volume as possible, in order that the size of the adsorption column may be kept at a minimum. For this particular work, silica gel appears to be better than the other adsorbents tested (section IV–5). The 28- to 200- and the 28- to 42-mesh sizes of silica gel have substantially the same adsorptive capacity (section IV–5), but the rate of filtration (unless auxiliary control is provided) is many times greater with the silica gel of larger particle size. As already mentioned, the more rapid the rate of filtration the greater the volume of pentane required, and the greater the tendency to produce irregularly shaped zones. For these reasons, the 28 to 200 mesh appears preferable for laboratory work, whereas for large-scale operation, where time is a major consideration, a larger size may be more desirable.

3. THE DISPLACING LIQUID

Any paraffin or naphthene hydrocarbon in the liquid phase with a boiling point well removed from that of the material under investigation may be used to displace the original paraffins and naphthenes. With hydrocarbons of the gasoline fraction, *n*-pentane, *n*-butane, or *n*-propane may be used. When the method is used on a laboratory scale, *n*-pentane is the most convenient displacing liquid.

4. THE DESORBING LIQUID

Almost any polar liquid which does not react with the hydrocarbons, the adsorbent, or the material of the adsorption tube may be used to desorb the aromatic hydrocarbons. For work on a laboratory scale, it is desirable that the desorbing liquid dissolve and carry the aromatic hydrocarbons in solution into the filtrate. It is also desirable that the desorbing liquid be completely soluble in water and preferentially less soluble in the hydrocarbon, in order that its removal from the hydrocarbon may be readily effected by extraction with water. Methanol, acetone, and water have been used as desorbing liquids in this laboratory.

Water readily effects the desorption of aromatic hydrocarbons, but they remain entrapped within the macroscopic interstices of the adsorbent. In this case, if the aromatics are not too high-boiling, they can be removed by the passage of steam. While this procedure may have some merit for large scale operation, it is inconvenient for laboratory work. Acetone also desorbs aromatic hydrocarbons, but

a number of washings with water are required to remove completely the acetone from the hydrocarbon portion.

Methanol is more satisfactory than water or acetone, since it dissolves the aromatic hydrocarbons and since a single extraction with water removes it almost completely from the hydrocarbon portion.

VII. PROCEDURE

The fraction by volume of aromatic hydrocarbon, c_a, and the volume of aromatic hydrocarbon, Q_{va} adsorbed per gram of adsorbent are determined for the petroleum fraction or mixture of hydrocarbons to be separated. The quantity of adsorbent required for the separation of a given volume of solution is then estimated (section 5), and this is charged into an adsorption column of the proper size. The mixture

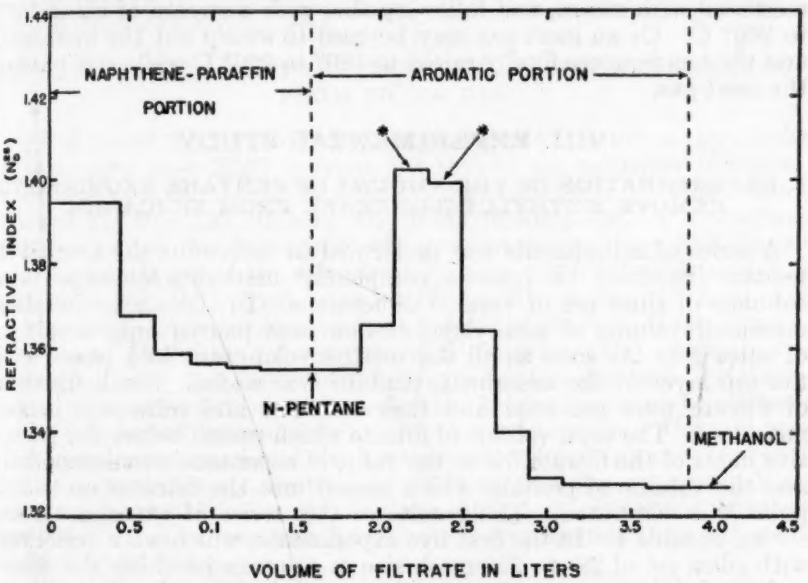

FIGURE 3.—*Results on the quantitative separation of the aromatic hydrocarbons in a known mixture of 17 pure hydrocarbons.*

The scale of ordinates gives the refractive indices of the fractions of filtrate, and the scale of abscissas gives the total volume of filtrate.

of hydrocarbons is allowed to filter through the adsorbent, and, as soon as the last of this material has entered the top layer of adsorbent, *n*-pentane is added and allowed to filter. It is desirable to use a substantial excess of pentane over that quantity which was estimated as sufficient to remove all the paraffins and naphthenes and which was used to estimate the quantity of silica gel required. As soon as the requisite amount of pentane has passed through the top layer of adsorbent, methanol is added to the column and allowed to filter. Fractions of filtrate are collected and their refractive indices determined. In figure 3 the refractive indices of the fractions resulting from a typical experiment are plotted with respect to the total volume of filtrate. This figure shows the decrease in refractive index from

that of the original naphthene-paraffin portion to that of pentane, then the increase as aromatic hydrocarbons appear in the filtrate, and finally, when all the aromatic hydrocarbons have been removed, the decrease nearly to the refractive index of methanol (see section VIII–3).

If a definite portion with the refractive index of *n*-pentane is not obtained, the operation is a failure and should be repeated with more pentane, or more silica gel, or both.

The naphthene-paraffin portion is distilled to remove the *n*-pentane. The aromatic portion is extracted once with water to remove the methanol and then distilled to remove *n*-pentane. If a small amount of methanol remains after the extraction, it will be removed as an azeotropic distillate with the *n*-pentane.[11]

At the end of an operation, the adsorbent contains only methanol and is readily reactivated. This can be done by sweeping out the methanol with steam, and following this with a stream of air at 180° to 200° C. Or an inert gas may be used to sweep out the methanol, and the temperature finally raised to 180° to 200° C while still passing the inert gas.

VIII. EXPERIMENTAL STUDY

1. DETERMINATION OF THE AMOUNT OF PENTANE REQUIRED TO REMOVE METHYLCYCLOHEXANE FROM SILICA GEL

A series of experiments was performed to determine the amount of pentane required to remove completely methylcyclohexane from columns of silica gel of various dimensions. In these experiments a measured volume of methylcyclohexane was poured onto a column of silica gel. As soon as all the methylcyclohexane had passed into the top layer of the adsorbent, pentane was added. Small fractions of filtrate were collected and their volumes and refractive indices measured. The total volume of filtrate which passed before the refractive index of the filtrate fell to the value of *n*-pentane was determined, and the volume of pentane which passed into the filtrates up to this point was computed. The results of this series of experiments are shown in table 1. In the first five experiments, which were performed with silica gel of 28- to 200-mesh size in columns in which the diameter varied between 4.27 and 1.03 cm and the ratio of length to diameter between 11.7 and 70.2, substantially the same ratio of pentane to silica gel, namely 0.28 to 0.33 ml per gram, was required. In experiments 6 and 7, silica gel of 28- to 42-mesh size was employed and a much higher ratio of pentane to silica gel was required, namely 0.60 to 0.76 ml per gram. The larger quantity required in this case is associated with more rapid filtration. In experiments 8 and 9, a stopcock at the bottom of the column was used to reduce the speed of filtration to a small fraction of the free rate. In this case the amount of pentane was reduced, and the values 0.35 and 0.48 per ml per gram were obtained. Unless the adsorption column has been provided with equipment to control the rate of filtration and unless the influence of this factor has been evaluated for the apparatus in question, adsorbent of 28- to 200-mesh size should be used for laboratory work.

[11] It is interesting to note that methanol displaces a small amount of water from the silica gel in the column, and this causes the appearance of two phases in certain of the filtrate fractions. The fractions indicated with asterisks in figure 3 contained two phases. (See also section VIII-3.)

TABLE 1.—*Amount of pentane required to remove methylcyclohexane[a] from silica gel*

Experiment number	Particle size of silica gel	Mass of silica gel	Volume of pentane	Dimensions of the column			Ratio: volume of pentane to mass of silica gel
				Length	Diameter	Ratio: $\frac{\text{length}}{\text{diameter}}$	
	Mesh	*g*	*ml*	*cm*	*cm*		*ml/gm*
1	28 to 200	31.08	9.00	50	1.03	48.5	0.29 ±0.03
2	28 to 200	65.10	18.7	50	1.52	32.9	.29 ± .03
3	28 to 200	170.4	56	50	2.43	20.6	.33 ± .03
4	28 to 200	485.0	154	50	4.27	11.7	.32 ± .03
5	28 to 200	108.4	30.5	99	1.41	70.2	.28 ± .03
6	28 to 42	29.9	18	50	1.03	48.5	.60 ± .05
7	28 to 42	62.9	8.3	50	1.52	32.9	.76 ± .05
8[b]	28 to 42	63.0	22	50	1.52	32.9	.35 ± .03
9[b]	28 to 42	158.8	76	50	2.43	20.6	.48 ± .03

[a] A sufficient amount of methylcyclohexane was used in each experiment, so that the first portion of the filtrate contained only methylcyclohexane.
[b] In experiments 8 and 9, the rate of filtration was reduced below that of free filtration by means of a stopcock at the bottom of the adsorption column.

2. RECOVERY OF METHYLCYCLOHEXANE-HEPTANE MIXTURE FROM SILICA GEL

A mixture of 365.3 g (505.9 ml), consisting of 47.33 percent by weight of *n*-heptane and 52.67 percent by weight of methylcyclohexane, was added to a column containing 2,000 g of silica gel.[12] This column of silica gel was 120 cm long and 5 cm in diameter. Pentane was added after all the heptane-methycyclohexane mixture had passed into the top layer of the adsorbent. After 1,125 ml of filtrate had been collected, the refractive index of the filtrate had fallen to that of *n*-pentane. (This corresponds to 619 ml of pentane in the filtrate, or 0.31 ml of pentane per gram of silica gel.) The pentane was separated from the heptane-methylcyclohexane mixture by distillation in an appropriate column, and the heptane-methylcyclohexane mixture siphoned from the still pot into a cold bottle. The still was washed with methanol and the heptane-methylcyclohexane recovered from the washings by removal of the methanol by extraction with water. The total mass of heptane-methylcyclohexane recovered was 362.9 g. The loss was 2.4 g, which corresponds to 0.7 percent of the original mass.

3. DETERMINATION OF THE AMOUNT OF METHANOL REQUIRED TO REMOVE TOLUENE AND "DIETHYLBENZENE" FROM SILICA GEL

Three filtration experiments were performed with 200 g of silica gel[13] in a 60-cm column 2.3 cm in diameter. In the first and second experiments, 15 ml of "diethylbenzene" and 15 ml of toluene, respectively, were added and allowed to percolate into the gel, and then methanol was added. In the third experiment, methanol alone was allowed to filter through the adsorbent. The results of these experiments are shown in figure 4, in which curves I, II, and III refer, respectively, to experiments 1, 2, and 3, and in which the refractive

[12] No. 859528–2000, see footnote 5.
[13] No. 859528–2000, see footnote 5.

indices of the individual filtrate fractions are plotted with respect to the volume of filtrate.

Curves I and II show that after a volume of filtrate of about 30 ml was obtained the refractive index of the filtrate fell nearly to the

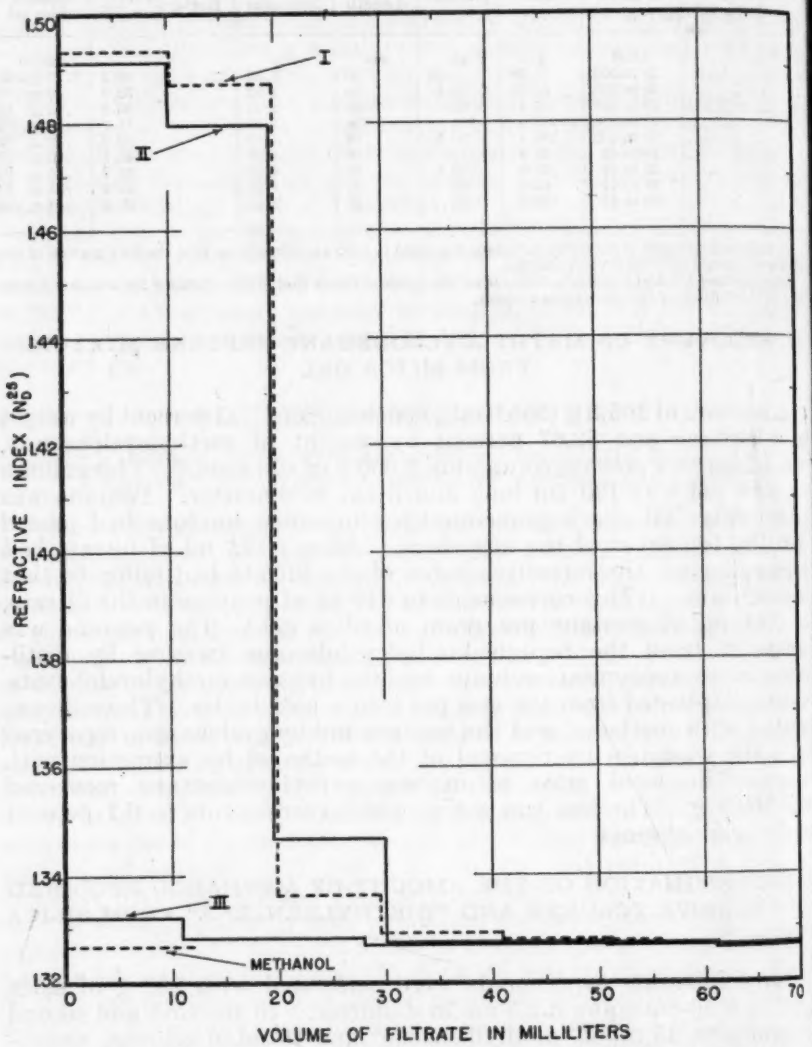

FIGURE 4.—*Results of experiments on the recovery of toluene and "diethylbenzene" from silica gel.*

The scale of ordinates gives the refractive indices of the frations of filtrate and the scale of abscissas gives the total volume of filtrate. Curves I and II refer to experiments in which "diethylbenzene" and toluene, respectively, were added to the adsorbent column and then methanol was added. Curve III refers to an experiment in which only methanol was added.

refractive index of methanol. The fractions representing that portion of the filtrate beyond 30 ml were free from hydrocarbon. The failure to reach the refractive index of methanol immediately after the re-

moval of the hydrocarbon was found to be due to the continued displacement of small amounts of water from the silica gel. The presence of water was evident in the second fractions from the first two experiments, in which two phases were observed. In experiment 3, in which methanol alone was filtered, the refractive index (n_D^{25}) of the first fraction was 1.3319, which may be compared with the values 1.3266 and 1.3325 for methanol and water, respectively. In general, fractions with refractive indices below about 1.329 are unlikely to contain hydrocarbon, but should in any case be tested by extraction with water.

4. RECOVERY OF TOLUENE FROM SILICA GEL

A weighed amount of toluene (approximately 15 ml) was added to a column containing 200 g of silica gel.[14] After all the toluene had passed into the top layer of silica gel, methanol was added. The filtrate was allowed to run into a weighed 125-ml separatory funnel containing 30 ml of water. After 30 ml of filtrate had collected, the total volume of water in the separatory funnel was brought to 85 ml, the separatory funnel was shaken and placed in a centrifuge, and the mixture centrifuged. The bulk of the aqueous solution was drawn off, the mixture again centrifuged, and the remainder of the aqueous solution drawn off. In this manner a sharp separation between the phases was obtained, and the walls of the separatory funnel were entirely free from water globules. The recovered toluene was weighed. The results of three such experiments, together with those of three blank experiments in which the same volumes of toluene, methanol, and water were shaken together in a separatory funnel and the toluene recovered and weighed, gave the following results: Loss of toluene in both adsorption and recovery, mean of three experiments, 0.35 ± 0.05 percent by weight; loss of toluene in the blank experiments, mean of three experiments, 0.14 ± 0.02 percent by weight; loss of toluene in the adsorption process alone, mean 0.21 ± 0.05 percent by weight.

5. SEPARATION AND RECOVERY OF A KNOWN MIXTURE OF AROMATIC HYDROCARBONS FROM A KNOWN MIXTURE OF NAPHTHENES AND PARAFFINS

A mixture of the 17 known hydrocarbons shown in table 2 was prepared quantitatively by weight. This mixture (about 2.3 liters in volume) was divided into four nearly equal portions, each of which was filtered through 4,200 g of silica gel,[15] contained in a 250-cm column, 5 cm in diameter. This was followed by the addition of 1,800 ml of *n*-pentane and then by the addition of methanol. The refractive indices of the fractions resulting from the filtration of one of these portions are shown in figure 3. The naphthene-paraffin portions and the aromatic portions from the four experiments were combined to make one naphthene-paraffin portion and one aromatic portion. The pentane and methanol were removed from each portion as described in section VII, and the remainder of each portion was distilled separately in a column of high separating efficiency. The values of boiling point and refractive index of the fractions of distillate as a function of the

[14] No. 859528–2000, see footnote 5.
[15] No. 859528–2000, see footnote 5.

volume and mass showed in each case excellent accord with the known composition of the material.[16] An indication of the completeness of the separation and of the material lost during the processes of adsorption and distillation is given in table 3.

The percentages of the total product recovered constituted by the aromatic portion and by the naphthene-paraffin portion recovered are 35.97 and 64.05, respectively, whereas the corresponding percentages representing the composition of the original material are 35.69 and 64.31. That is to say, the percentage by weight of the aromatics in the material recovered differs from that in the material charged by only 0.3 percent.

TABLE 2.—*Data on the 17 pure hydrocarbons used in making up the known "test" mixture*

Compound	Boiling point	Mass		
		Paraffin	Naphthene	Aromatic
	°C	g	g	g
2-Methylpentane	60.3	57.79		
n-Hexane	68.7	97.39		
Benzene	80.1			86.40
Cyclohexane	80.7		158.90	
n-Heptane	98.4	132.97		
Methylcyclohexane	100.9		141.47	
Toluene	110.6			94.10
n-Octane	125.7	105.64		
Ethylcyclohexane	131.8		62.17	
Ethylbenzene	136.2			87.40
p-Xylene	138.4			89.44
m-Xylene	139.1			88.94
o-Xylene	144.4			73.80
n-Nonane	150.8	110.46		
Isopropylbenzene	152.4			104.77
n-Propylcyclohexane	156		115.19	
n-Decane	174.0	144.03		
Total		648.28	477.73	624.91

TABLE 3.—*Results on the quantitative separation and recovery of the aromatic hydrocarbons in a known mixture of 17 pure hydrocarbons*

Material	Charged		Recovered		Loss	
	Mass	Percentage	Mass	Percentage	Mass	Percentage
	g		g		g	
Aromatics	624.91	35.69	617.71	35.28	7.20	0.41
Paraffins+naphthenes	1,126.01	64.31	1,099.66	62.80	26.55	1.51
Total	1,750.92	100.00	1,717.37	98.08	33.55	1.92

IX. DISCUSSION OF THE SEPARATION OF HYDROCARBONS BY ADSORPTION

The method of separating aromatic hydrocarbons from naphthenes and paraffins by adsorption has the following desirable features: (a) the simple type of the apparatus required; (b) the quantitative nature of the separation which can be obtained; and (c) the applicability of the method to material of very wide boiling range, such as the entire gasoline or kerosine fractions of petroleum.

[16] A report on the analysis of the fractions from this distillation is given elsewhere [15].

The separation of aromatic hydrocarbons from naphthenes and paraffins is only one of several separations which, by the choice of proper conditions, can be accomplished by the use of the adsorption method. Winterstein and coworkers [3, 5] have shown that various polynuclear aromatic hydrocarbons may be separated from each other. These authors have found that for aromatic hydrocarbons consisting of condensed rings arranged linearly those with the greater number of rings are the more strongly adsorbed, while for other aromatic hydrocarbons consisting of condensed rings, the arrangement of the rings influences the order of their adsorption. Thus they found that naphthacene, with four rings per molecule arranged linearly, is more strongly adsorbed than 1,2-benzpyrene with five rings per molecule arranged nonlinearly. The presence of olefinic linkages also influences the order of adsorption; in general the greater the number of olefinic linkages, other things being equal, the more strongly the substance is adsorbed [3]. Observations made in this laboratory show that monoolefins are selectively adsorbed from naphthenes and paraffins of corresponding molecular weight [7, 11]. The results of these investigations may be summarized by the statement that, with certain limitations on the type and configuration of the aromatic rings, and with the restriction to compounds of approximately equal molecular weights, the arrangement of hydrocarbons in order of their decreasing adsorbability is as follows: 4-, 3-, 2-, and 1-ring aromatic hydrocarbons, diolefins, monoolefins, naphthenes, and paraffins.

X. REFERENCES

[1] M. Tswett, Ber. deut. botan. Ges. **24,** 316 (1906); **24,** 384 (1906).
[2] H. H. Strain, Chromatographic Adsorption Analyses, p. 21–24 (Interscience Publishers, Inc., New York, N. Y., 1942).
[3] R. Kuhn and A. Winterstein, Helv. Chim. Acta **11,** 87, 116, 123, 144 (1928).
[4] A. Winterstein and K. Schön, Z. physiol. Chem. **230,** 146 (1934).
[5] A. Winterstein, K. Schön, and H. Vetter, Z. physiol. Chem. **230,** 158 (1934).
[6] B. Tarasov, Azerbaĭdzhanskoe Neftyanoe Khoz. **1,** No. 10, 47–50 (1926).
[7] B. J. Mair and J. D. White, J. Research NBS **15,** 51 (1935) RP809.
[8] B. J. Mair and S. T. Schicktanz, J. Research NBS **15,** 557 (1935) RP 849
[9] C. B. Willingham, J. Research NBS **22,** 321 (1939) RP1185.
[10] B. C. Allibone, J. Inst. Petroleum **27,** 94 (1941).
[11] B. J. Mair and A. F. Forziati, J. Research NBS **32,** 151 (1944) RP1582.
[12] H. G. Cassidy, J. Chem. Education **16,** 88 (1940).
[13] J. N. Wilson, J. Am. Chem. Soc. **62,** 1583 (1940).
[14] H. G. Cassidy, J. Am. Chem. Soc. **62,** 3073 (1940); **62,** 3076 (1940); **63,** 2628 (1941).
[15] F. D. Rossini, B. J. Mair, A. F. Forziati, A. R. Glasgow, Jr., and C. B. Willingham, Proc. Am. Petroleum Inst. **23,** (III), 7 (1942); Oil Gas J. **41,** No. 27, 106 (1942); Petroleum Refiner **21,** No. 11, 73 (1942).

WASHINGTON, *September 29, 1942.*